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# Water Quality Research Status Report—1992

Beltsville Agricultural  
Research Center,  
Natural Resources Institute

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## Executive Summary

Over the last 3 years several laboratories in the Natural Resource Institute have been involved in research on issues related to groundwater quality. Results for calendar year 1992 are given in this report. Some of the significant results from this research since 1990 are:

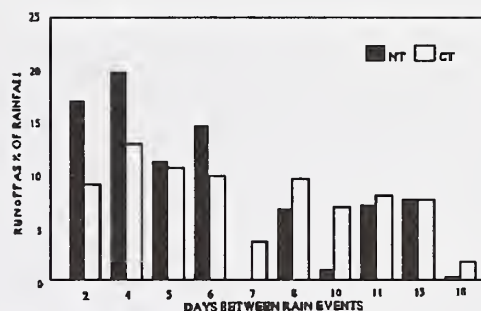
- Developed a Pesticide Properties Database (PPD) of chemical and physical properties of commonly used pesticides for use by Soil Conservation Service, modelers, and others to predict the potential of various pesticides to move to the groundwater.
- Developed NUMEX, a combined expert system and laboratory information system for soil testing laboratories that can be used to make recommendations to farmers about nutrients application, thus leading to a significant reduction in nutrient leaching.
- A soil N test for corn was evaluated and successfully deployed in Maryland which measures the  $\text{NO}_3\text{-N}$  concentration in the surface foot of soil when corn is 6-12 inches tall, thus allowing the farmer to adjust future fertilizer N application accordingly. The test can successfully identify N sufficient sites and is being tested in Maryland to prevent over-fertilization and reduce  $\text{NO}_3\text{-N}$  losses to groundwater and the Chesapeake Bay.
- Grass winter cover crops are better recyclers of corn fertilizer N than legumes. Rye recovered 50-60% of the residual fertilizer while hairy vetch or crimson clover recovered less than 10%. Grass cover crops should thus reduce nitrate loss into groundwater and the Chesapeake Bay. The Maryland Department of Agriculture has recently included grass cover crops for N assimilation as a cost share practice in their Maryland Agriculture Cost-share (MACS) program.
- Found large seasonal changes in water infiltration rates and associated potential for rapid deep-percolation losses by preferential flow during seasons of high infiltration rates.
- Demonstrated that a granular starch-encapsulated herbicide dramatically reduced herbicide leaching (relative to technical grade) from no-till field cores subjected to preferential flow conditions.
- Demonstrated that preferential herbicide transport on a field-scale can take place under both no-till and conventional tillage. However, shallow herbicide transport was greater under no-till management in a Coastal Plain soil.
- Demonstrated that soil residue values by themselves are a poor indicator of field-scale herbicide behavior.
- Developed a pretreatment extraction methodology for starch-encapsulated materials, that for the first time, allows quantitative analysis of starch-encapsulated herbicides. Methodology is now being used in a seven state water quality research project.
- Demonstrated that preferential transport of surface broadcast herbicides could be a significant contributor to shallow ground water pollution ( $\sim 1$  m). Use geostatistical analysis to define



tillage practices that were contributing to groundwater contamination.

- Determined soil physical properties and characteristics which are critical in obtaining estimates of soil water retention.
- Determined the release characteristics of starch encapsulated atrazine and alachlor as a function of water potential, temperature and biological activity. Determined that herbicide release characteristics are governed by a diffusion process.
- Evaluated volatility of commercial and starch-encapsulated atrazine and alachlor in bare soil ecosystem chambers under three soil temperatures. Demonstrated that volatilization losses of starch-encapsulated atrazine was an order-of-magnitude less than for the commercial formulation. Relative to the commercial formulation, the starch-encapsulated alachlor had greater volatilization losses.
- Field-scale mobility and persistence of commercial and starch-encapsulated atrazine and alachlor were determined. Starch-encapsulated atrazine, its release being governed by a diffusion process, exhibited a dramatic reduction in mobility, and an increased persistence. The reduction in atrazine mobility was attributed to atrazine movement into the smaller pores of the soil matrix, where it is less susceptible to preferential transport.
- Field-scale volatilization losses of commercial and starch-encapsulated atrazine were evaluated under both conventional and no-till practices. Herbicide volatilization losses were initially higher (<6 d) under no-till. However, rain events washed the commercial formulation below the surface litter which created a stagnant vapor boundary, reducing volatilization losses. Starch-encapsulated volatilization losses were much less than the commercial formulations.
- Compared volume-averaged leachate levels of atrazine, alachlor, bromide and nitrate below the active root zones of conventional and no-till fields (using suction lysimeters at 1.5 & 1.8 m). Bromide data indicates that preferential transport was sampled for both tillage practices. Herbicide and nitrate levels were much lower under no-till than conventional tillage. Reduced herbicide levels under no-till attributed to enhanced biological activity in the preferential flow pathways, while annual soil disturbance in conventional tillage minimizes/eliminates the accumulation of organic material in preferential flow pathways.
- The concentration of pesticides in the surface soil is lower under no-till than under conventional till production practices.
- A root zone model (PRZM) simulation with field data for atrazine showed good agreement for the top 10 cm soil depth in conservation till plots but underestimated concentration for the no-till plots. (PRZM does not account for preferential flow).
- Analysis of 3 years' field data showed that even a subtle difference in rainfall distribution (temporal) can result in marked spatial variability in the distribution of atrazine.
- Two years' runoff data showed greater amounts of water runoff from no-till than for conservation till when the time between rainfall events was >7 days, but less when <7 day passed between rain events.

- Laboratory studies have shown that: 1) pesticide leaching potential is higher at high compared to low rainfall intensities; 2) increasing the amount of crop residue decreases leaching; and 3) living vegetation is more effective in reducing leaching than dead vegetation.
- Determined s-Triazine ozonation product profile and relative rates; final product mineralization was achieved by a field tolerant microorganism.
- Found a direct correlation between fish liver lesions measured with classical histological methods and those measured with magnetic resonance imaging and spectroscopy.
- Found in vitro metabolic controls which increase photosynthate partitioning into foliar starch response to nitrogen limitation of soybean plants.
- Groundwater possesses low levels of mutagenic activity vs. soil leachates which possess much higher levels of activity, thus percolation through soil appears to play a crucial role in reducing the level of activity between the two zones.



## Preface

This is the third annual report of progress on water quality research in the Natural Resources Institute, Beltsville Agricultural Research Center, Agricultural Research Service, U. S. Department of Agriculture. The thrust of much water quality research has been the potential public health issue arising from the detection of trace amounts of agricultural chemicals in ground and surface waters. A recent Gallop poll of 1200 farmers throughout the U.S. showed that 92% will use safer pesticides in the future and most predict they will likely use fewer pesticides. The poll also revealed that 80% of the farmers expect the government to become increasingly involved with the environmental aspects of agriculture.

As more data is collected, it is apparent that the concern can be directed to specific agricultural chemicals, i.e, the organic herbicides and nitrates. The former are of concern because of high useage in crop protection programs, the latter because of frequent detections in water samples. While public health remains a paramount issue, there are unique regional problems that also are emerging as critical to the whole water quality issue. Extensive modeling efforts in the Cheaspeake Bay, the nations largest estuary, reveal that anoxia caused by eutrophication is serious impairing living resources in the Bay. A 40% nutrient reduction goal by the year 2000 is calculated to increase the oxygen tension in the deep recesses of the Bay. To accomplish is goal, 218 million tons of nitrogen and 15 million tons of phoshorus that enter the Bay annually must be eliminated. The major source of nonpoint pollution is associated with agriculture. To acheive this reduction, agricultural practices in the Northeast would have to be drastically altered. Now the water quality issue takes on not only the public health issue, but our whole farming system appraoch to food and fiber production. While now confined to the Northeast, strategies developed to alleviate the agricultural burden could be widely adapted in other parts of the nation. Far more challenging issues face the research community in acheiving various goals in our clean water programs.

Philip C. Kearney  
Institute Director  
Natural Resources Institute



# **Water Quality Research Status Report--1992**

## **Beltsville Agricultural Research Center, Natural Resources Institute**

compiled by Jerry C. Ritchie

### **Introduction**

This report covers the activities of scientists in the Natural Resources Institute, Beltsville Agricultural Research Center, who are involved in research related to water quality. The report has been divided into four (4) section.

**Section 1** covers the research accomplished in CY 1992. A short narrative of the purpose, accomplishment, and application of the different research is given. These narratives have been adapted from the 1992 CRIS Annual Reports.

**Section 2** contains a list of papers published or accepted for publication in 1990-1992.

**Section 3** contains a list of papers with interpretive summaries and technical abstracts that have been reviewed and approved for publication by ARS in 1991 and 1992. These summaries are taken verbatim from the ARS TEKTRAN (Technology Transfer Automated Retrieval System).

A search for "groundwater" papers in TEKTRAN listed 106 papers by ARS scientists for the period between January 1991 and January 1993 with 20 (19%) authored or co-authored by BARC scientists. However, I found 59 paper on groundwater by BARC scientists that have been approved and are available through the TEKTRAN system for the two year period.

**Section 4** contains a list of scientists with addresses and phone numbers.

BARC scientists are actively involved in research to help better understand and manage water quality. Research is underway to (1) develop data bases, (2) develop expert systems, (3) develop and validate models, (4) measure and understand N and pesticide transport, (5) measure and understand volatilization and its impact on chemical loss, (6) develop methods to biodegrade pesticide wastes, (7) develop management systems to minimize N and pesticides loss from agricultural fields, (8) studies of biological effects, and 9) develop basic and theoretical understanding of chemical transport in agricultural, riparian, and natural ecosystems.

## Section 1--Research Accomplishments 1991

### 1992 Research Summaries of Water Quality Research at BARC

#### Water Quality Monitoring Fish Liver Sentinels Using MRI/MRS

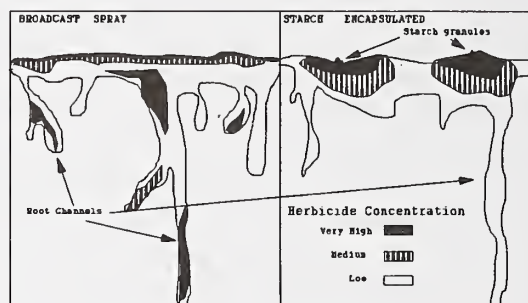
Water quality studies continue at BARC using magnetic resonance imaging (MRI) and spectroscopy (MRS). The *in vivo* and *in vitro* MRI/MRS procedures show a measure of success that is encouraging. Hepatocarcinomas, eosinophilic foci, basophilic foci and fluid-filled cysts have been delineated by displaying the data in a magnetic resonance *relaxation map form* and confirmed by histology. This approach is important to build a data base that establishes a correspondence between a MRI/MRS data and established pathologies for a given water pollutant. The ultimate objective is to use the MRI/MRS approach to determine the early liver tissue response to a particular pollutant or metabolic product (xenobiotic).

CRIS 0500-00038-007-00D/Gassner

#### Minimizing Preferential Transport of Pesticides Through Diffusion

Preferential pesticide transport is a convective process which results in the rapid movement of pesticides through agricultural soils. By increasing the role of diffusion in chemical transport, preferential movement may be reduced. A controlled release formulation that releases atrazine into the soil environment through a diffusion process was compared to a commercial formulation on no-till and conventionally tilled corn fields. Atrazine applied as the controlled release formulation was more persistent but mobility was also dramatically reduced when compared to commercial atrazine. These results suggest that new formulations or management practices that allow chemical diffusion to play a more important role may reduce chemical leaching to groundwater.

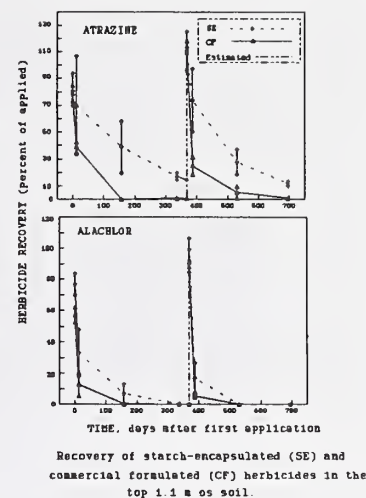
CRIS 1270-13000-005-00D/Gish/Wienhold



Effect of herbicide diffusion on the movement of starch-encapsulated and commercially formulated herbicide through soils.

## Behavior Assessment of Starch-Encapsulated Alachlor and Atrazine

To evaluate environmental impact of new or currently available herbicide formulations, a number of complex processes must be quantified. Laboratory and field studies were conducted to compare behavior of starch-encapsulated to commercial formulations of atrazine and alachlor. Starch-encapsulation (SE) dramatically increased herbicide persistence. When compared to the commercial formulations the mobility of SE-atrazine was dramatically reduced while that of alachlor was not significantly effected (based on soil core and solution samples). Field atrazine volatilization on conventionally tilled field was similar to those fluxes observed in bare soil ecosystem chambers. Although early volatilization fluxes were greatest under no-till, after thirty-five days, no-till volatilization losses were much less than those observed under conventional tillage. The reduction in herbicide volatilization under no-till was attributed to early rains that may have washed the herbicide below the surface litter. To reduce persistence, additional studies comparing persistence and efficacy as a function of granule size and application rate have been initiated.



CRIS 1270-13000-005-00D/Gish/Wienhold

## Mechanistic Studies Provide Details to Optimize Pesticide Waste Remediation

A remediation scheme for pesticide contaminated matrices involves ozonation followed by biomineralization. Ozonation reaction profiles and relative rates for atrazine, simazine, propazine and their degradation products have been determined. The proposed mechanism suggests that more oxidant may be needed if certain pathways are preferred over others, potentially impacting the overall efficiency. Complete mineralization of the final ozonation product of all three herbicides has been demonstrated using DRS-I, an organism isolated to tolerate field conditions. A prototype unit was fabricated from readily available materials and consists of an ozonation reactor, equipped with ozone monitor and flow controllers to quantitate efficiency and an ozone kill unit to destroy residual ozone in the effluent gases, and two vessels for optimal biological treatment. A new solid support in the fixed film bioreactor vessel that can moderate pH changes is being tested in collaboration with W.R. Grace Co. The results of this research will provide scientists, action agencies and industries with a framework for alternative strategies to remediate pesticide wastes.

CRIS Nos. 1270-12130-006-00D and 0500-00026-014-00D/Hapeman/Shelton



## **ARS Pesticide Properties Database (ARS-PPD)**

The ARS-PPD lists those chemical and physical properties of common pesticides that determine how likely they are to pollute water supplies. The database is for use by managers and advisors, especially officers in the Soil Conservation Service, to predict the potential of various pesticides to move into groundwater under a range of weather and soil conditions. The ARS-PPD was expanded from 92 to 230 pesticides by adding the database developed by Dr. R. Don Wauchop, after checking all data and references. The database was distributed to the pesticide manufacturers via the National Agricultural Chemicals Association for checking. To guide further development of PPD, a steering committee was appointed consisting of representatives from NACA, SCS, EPA, ES, USGS, NPS, and ARS. A brochure for advertising the PPD was prepared. The ARS-PPD constitutes a single source of reliable information for ARS and SCS researchers using models to design management practices that minimize pollution.

CRIS 0500-00026-003-00D/Herner/Acock

## **Effect of Tillage Practice on Herbicide Leaching to Groundwater**

No-till (NT) cultural practice may increase the leaching potential of pesticides compared to conventional-till practices. NT and CT field plots were uniformly treated each year with several pesticides and the amount of pesticide leaching was monitored through analysis of groundwater samples taken from a network of 1.5 to 11m deep wells. Concentrations of pesticides were cyclical; residues were highest soon after application each year (1986-1991) and then declined, alachlor and cyanazine to nondetectable levels within 3 mo. Atrazine residues were always higher under NT than CT, but differences were small except in 1988 when a large rain event occurred soon after application. Results from 1988 indicated that preferential transport occurred. Results of this study indicate that timing and amount of rainfall relative to pesticide application are the primary factors controlling pesticide leaching.

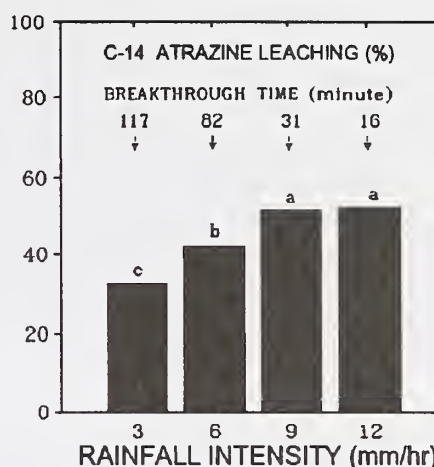
CRIS 1270-12130-003-00D/Isensee/Sadeghi

## Impact of Rainfall Intensity and Crop Residue on Atrazine Leaching

The effect of rainfall intensity and vegetative cover on pesticide leaching is not well understood, particularly under conservation tillage. Undisturbed soil cores taken from the surface horizon of a NT field were treated with atrazine and subjected to simulated rainfall at 3 to 12 mm/h. The crop residue on the surface of another set to soil cores was adjusted from 0 to 100% of average field levels, treated with atrazine and subjected to simulated rainfall at 9 mm/h. Increasing rainfall intensity increased total amount of atrazine leached; initial rate of leaching was higher at the higher rainfall intensities. Increasing amount of crop residue decreased atrazine leaching by 25 to 37%

compared to no crop residue; freshly harvested vegetation decreased leaching 20% more than dead crop residue. Results are useful for pesticide leaching models and crop residue data indicate that amount of dead and living vegetation on soil surface at spraying time may significantly affect pesticide leaching potential.

CRIS 0500-00032-004-00D/Isensee/Sigua



## Repeated DNA-Element Associated with s-Triazine Degradation Genes

Microbial degradation plays an important role in the dissipation of pesticide molecules from the environment. Soil microbes have shown a great ability to evolve the enzymes and pathways required to degrade pesticides. *Pseudomonas* species strain A (NRRLB12228) is capable of completely degrading simple s-triazine compounds (chemical substituents of the herbicides atrazine, simazine, and cyanazine), utilizing them as a source of nitrogen for cell growth. Restriction endonuclease mapping of cloned DNA containing the genes which encode s-triazine degradation enzymes in strain A revealed the presence of a repeated DNA element around which a high degree of DNA recombination seems to be occurring. The nucleotide sequence of this element was determined and compared to sequences in the GENBANK database. These examinations suggest that this repeated DNA element is a new bacterial insertion element. Such elements are known components of bacterial transposons or 'jumping genes' and may play a key role in the evolution and spread of pesticide degradation traits in soil microbes.

CRIS 1270-12130-005-00D/Karns



## **Numex: a Nutrient Management System**

The most immediate way of reducing water pollution by agricultural chemicals is to advise farmers what we know already empirically about preventing pollution. NUMEX is a combined expert system and laboratory information system for soil testing laboratories that makes recommendations to the farmer about the nutrients to apply in order to feed the crop, and how to apply them without contaminating surface and groundwater. First developed for Maryland, NUMEX has now been adapted for use in Nebraska and Iowa by encoding decision making rules used by experts in each of those states. Documentation and users guides have been written and the code delivered to the soil testing laboratories. The recommendations of NUMEX will be mailed out to farmers as part of their soil test reports, and, when the expert knowledge is applied, there should be a significant reduction in nutrients leaching into groundwater.

CRIS 0500-00032-019-00D/Lemmon

## **Nitrogen Soil Test Evaluated**

Residents of the Mid-atlantic region are concerned about nitrate pollution of groundwater and the Chesapeake Bay. A basic tool to increase nitrogen (N) use efficiency is a N soil test. A N soil test for corn was evaluated in Maryland which measures the nitrate N concentration in the top foot of soil when the corn is 6-12 inches tall i.e., about two weeks before planned sidedressing. The test was evaluated on research farm experiments over a wide range of soils and over several growing seasons. These tests studied the effects of tillage, applications of manure or composted sludge, winter cover crops, and applications of fertilizer N on soil nitrate-N contents and corn grain yields. The results show that soil N test can successfully identified N sufficient sites i.e., sites which need no additional fertilizer. Nitrogen sufficient sites contained greater than 22 ppm nitrate-N and were usually associated with previous inputs of manure or composted sludge, or had grown legume cover crops. The accuracy of the test was not affected by tillage practices. This soil N test is most useful for manured fields where uncertainties in application rates and N losses make N management very difficult. This test is being used by Maryland extension agents, nutrient management consultants, and farmers to identify N sufficient sites and thereby conserve fertilizer N and reduce nitrate losses to groundwater and the Chesapeake Bay.

CRIS 1270-12130-004-00D/Meisinger

## **Characterization of a New s-Triazine Degradation Gene**

The widespread use and relative persistence of s-triazine compounds such as atrazine has lead to increasing concern about surface and groundwater contamination by these compounds. Unfortunately, biodegradation studies have yielded very few microbial isolates that transform s-triazines. However, one bacterium, Rhodococcus corallinus, has been shown to have an enzymatic activity that catalyzes the dechlorination of the s-triazine deethylsimazine (CEAT). We seek to manipulate this enzymatic activity for degrading s-triazine compounds. As a first step in this process, we determined the nucleotide sequence of a 2.4 kilobase DNA fragment that contains the CEAT hydrolase gene, trzA. We are now using this information to alter the gene so that it can be expressed in other useful bacterial strains. Since dechlorination is frequently the rate limiting step in the biodegradation of pesticides, manipulation of this gene will provide us with a new biological tool to degrade solutions containing s-triazines.

CRIS: 1270-12130-005-00D/Mulbry/Seffens

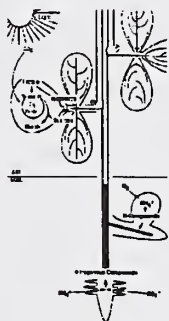
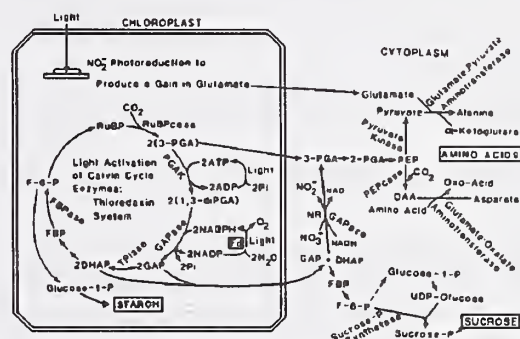
### Sources of Mutagenic Substances in Ground and Surface Water

Organic residues were extracted from surface water and groundwater samples from areas varying in intensity of agricultural activity. Commercially available, C-18 bonded silica solid phase tubes appear to work well for the extractions. Solvent eluates of the tubes were assayed using SOS microplate assay (SOSMA) for determining mutagenic activity. There was considerable variability, both temporally and spatially, in the activities of the more than 150 samples which were assayed. Low levels (about 2x background) of activity were detected in waters from several sites. The C-18 extracts of soil leachates have been tested and found to exhibit levels of activity in the range of 20-500 times background level. HPLC analyses of extracts indicate two general classes of compounds are present. One class contains highly polar and long wavelength-absorbing compounds [210-400 nm (approx.)] and the other class of compounds are less polar and absorb at short wavelengths (310 nm).

CRIS 0500-00038-007-00D/Rice/Pfeil

## Soybean Leaf Photosynthetic Metabolism Adjusts to Support Symbiotic N<sub>2</sub> Fixation During External Nitrogen Limitation

Leguminous plants, e.g. soybeans, are able to symbiotically assimilate atmospheric  $N_2$ , thus minimizing  $NO_3^-$  and  $NH_4^+$  fertilizer requirements for plant growth and bean development. During the onset of symbiosis, we found that young *Bradyrhizobium japonicum* infected soybean plants often displayed symptoms of nitrogen limitation including reduced leaf chlorophyll and soluble protein. However, these plants maintained foliar  $CO_2$  assimilatory rates sufficient to provide adequate fixed carbon for metabolic support of the bacteroides as well as the growth and maintenance of symbiosis.  $N_2$ -fixing soybeans displayed elevated foliar



soluble protein levels when compared with  $\text{NO}_3^-$ - and  $\text{NH}_4^+$  supported plants. In leaves of the  $\text{N}_2$ -fixing plants, both activities of starch synthesis pathway enzymes and hexose phosphate substrates of these enzymes increased. The net result was that there was a preferential partitioning of newly assimilated carbon photosynthate into starch and sugar. Positive metabolite effectors of starch synthesis pathway enzymes increased, and appeared to play a role in modulating increased starch synthesis enzyme activities. It was concluded that foliar photosynthetic partitioning was controlled and adjusted to support the bacterial component during the establishment of the symbiosis as well as to conserve reserve carbohydrates in the leaf until which time they could be metabolized to support amino acid and protein synthesis. These results will benefit crop physiologists and

agronomists whose mission it is to develop nitrogen fertilizer recommendations for crops that are grown in soils where there is potential danger of ground water contamination.

CRIS 1270-21000-014-00D/Robinson



## **Measurement and Modeling of Pesticide Fate in No-Till and Conventional Tillage Practices**

Comparison of the PRZM (Pesticide RootZone Model) simulations with the three years (1987-1989) atrazine residue data collected from our field plots showed a good agreement for the 0 to 10 cm soil depths in the conventional tillage Plots, but underestimated for the no-till Plots. Overall, the model estimation of atrazine residues for the lower soil depths in both tillage practices were significantly lower than the measured values, especially in the no-till plots. These PRZM simulations were based primarily on the estimated values of runoff and evapotranspiration, the two main components of the water balance in PRZM model. Model simulations are underway using the data collected since 1990, where runoff and evapotranspiration rates at the field site have been monitored.

CRIS 1270-12130-003-00D/Sadeghi/Isensee

## **Pesticide Sorption and Bioavailability**

Pesticides are increasingly being found in trace quantities in groundwater. Most process oriented models (i.e., PRZM) which predict leaching of pesticides to groundwater are dependent on accurate estimates of soluble (bioavailable) vs. sorbed ( $K_d$ ) pools. A new method has been developed which allows for independent estimation of soluble and sorbed pools in field moist soils. This method is being used to obtain more reliable estimates of atrazine sorption ( $K_d$ ) as a function of soil organic matter content. This, in turn, will allow for more accurate predictions of atrazine leaching to groundwater.

CRIS 0500-00032-004-00D/Shelton/Sadeghi

## **Variation in Denitrification in Riparian Zones**

Two cluster-well field experiments were conducted in 1992 as part of research to develop new field techniques for assessing the activity and potential for riparian areas to remove nitrates from shallow groundwater. A major observation from these experiments was that the nitrate injected into laterally flowing shallow groundwater moved i) without being degraded or transformed in the absence of added carbon substrate, but ii) was quickly denitrified when glucose-C was added at the same molar concentrations as the nitrate-N. This research shows that even though the potential for denitrification may exist in riparian areas, the lack of an available carbon energy source can result in very little actual transformations of nitrate.

CRIS 1270-13000-003-00D/Starr

## **Mobility of Agrochemicals Through Soil from Two Tillage Systems**

A series of laboratory studies was conducted to characterize the impact of two contrasting tillage systems on the movement of nitrate and four pesticides in soil. The two tillage systems were plow-(PT) and no-tillage (NT) for corn (*Zea mays*, L.) production. The study included incubation and leaching of undisturbed soil columns and disturbed soil samples from 16-yr plots subject to the two tillage regimes. Results of this study showed greater ponded flow movement of all agrochemicals in undisturbed soil columns from PT vs. NT conditions. Strong evidence was found for preferential flow through the soil, with the chemicals by-passing much of the soil-matrix under recently plowed soils as well as no-till soils. Caution should be exercised in generalizing from laboratory columns to field conditions, but these data suggest that there can be as great and greater leaching losses of surface applied agrochemicals to groundwater under PT than under NT.

CRIS 1270-13000-003-00D/Starr/Meisinger

## 2D Soil—a Model of Soil Processes and Root Growth

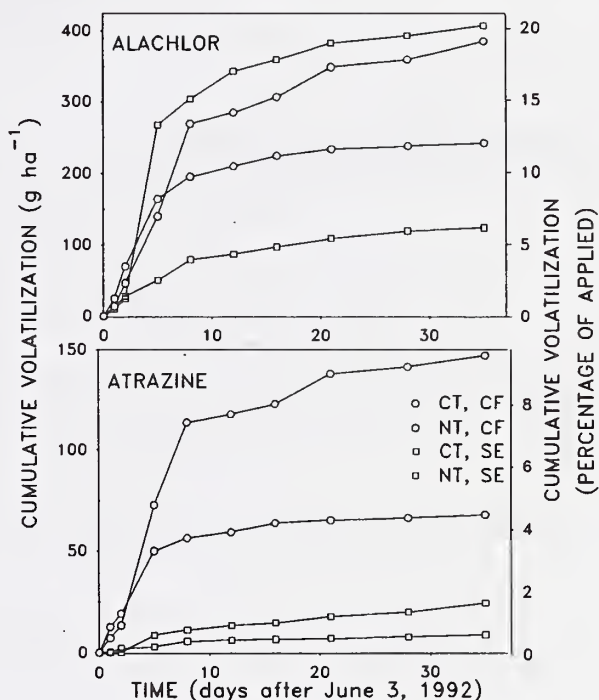
Most of the models currently used to simulate the movement of agricultural chemicals through soil are one dimensional and fairly simple. There are clear differences in water and solute movement under crop rows and between those rows. Our objective is to develop a comprehensive 2-D model of soil processes and root growth and link it to some of the best crop models available. After acquiring SWMS\_2D from the ARS Salinity Lab, the model was recast in modular form and modules for root growth, root water uptake, root solute uptake, root respiration, soil temperature, and gaseous diffusion were added. The code was modified to allow for the movement of several solutes simultaneously. The new model, 2DSOIL, was documented and released to interested researchers. 2DSOIL added to a crop model will give us a research tool to improve our management of agricultural chemicals.

CRIS 0500-00032-030-00D/Timlin/Pachepsky

## Diffusion of Atrazine and Alachlor in Agricultural Soils

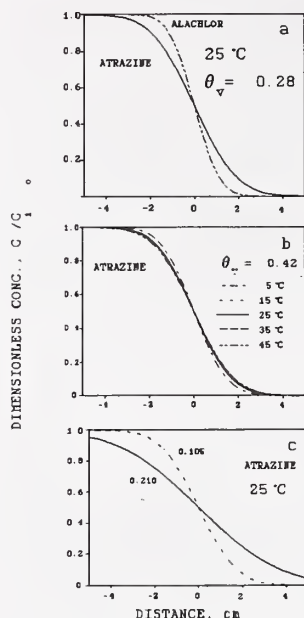
Diffusion is one of the processes whereby chemicals are transported in agricultural soils. Quantitative information concerning factors which influence the diffusive movement of agricultural chemicals is lacking. A laboratory study was conducted to quantify the effect of temperature and water content on diffusion of atrazine and alachlor in three soils with differing clay and organic matter contents. Atrazine diffused more rapidly than alachlor, likely because alachlor is more strongly adsorbed by soil than is atrazine. As temperature increased diffusive movement of both chemicals increased. As water content increased in a give soil, diffusive movement increased, likely because of a reduction in the tortuosity of the diffusion pathways. These results improve our understanding of the role of diffusion in movement of agricultural chemicals.

CRIS 1270-13000-005-00D/Wienhold/Gish



Cumulative volatilization of atrazine and alachlor applied as either commercial formulation (CF) or starch encapsulated (SE) formulation from conventionally tilled (CT) and no-till (NT) fields.

## Volatility of Surface Applied Atrazine and Alachlor



Herbicide diffusion transport as a function of herbicide chemistry (a), temperature (b) and soil volumetric water content (c).

Volatilization of pesticides is one process whereby agriculturally applied chemicals may enter into parts of the environment where they were not intended. A previous greenhouse study demonstrated that starch encapsulation (SE) reduced volatilization of atrazine and enhanced volatilization of alachlor when compared to the commercial formulation (CF). A study was conducted to extend these results and to compare volatilization from conventionally tilled and no-tilled fields. For each formulation volatilization losses of atrazine and alachlor were greater from conventionally tilled fields than from no-tilled fields; SE reduced volatilization of atrazine from both tillage practices; volatilization of alachlor from conventionally tilled fields was similar for both formulations; volatilization losses of SE alachlor were one-half those of commercial alachlor from no-till fields. These results suggest that SE may reduce volatilization losses of atrazine and alachlor, especially from no-till fields.

CRIS 0500-00032-004-00D/Wienhold/Gish



## **Section 2--Publications 1990-1993**

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## **Section 3--ARS Approved Publications 1990-1993**

### **ARS TEKTRAN (Technology Transfer Automated Retrieval System) Publications**

#### **MODELING APPROACHES FOR PREDICTING CROP ECOSYSTEM RESPONSES TO CLIMATE CHANGE**

**ACOCK BASIL, ACOCK MARY C**

**Interpretive Summary:** Climate change will result in combinations of soil, climate, and carbon dioxide concentration [CO<sub>2</sub>] that have not been experienced previously. The only realistic way of predicting how crop ecosystems will change, is to simulate future conditions using mechanistic crop and climate models. These models all have known defects so only give a crude indication of what might happen. Also, farmers and agronomists have a long record of adapting crop ecosystems to changing conditions. There is a wide range of genetic material in the available crop species and cultivars that can fit almost any ecological niche. The farmer can also change his management practices such as planting and harvesting date, plant population density, fertilization and irrigation. Looking at the available germplasm from a modelers point of view, we can identify differences in how phenology and photosynthesis, or dry weight gain, respond to temperature and daylength. We can also identify optimum temperature ranges and extremes which will destroy a crop. This information is not readily available but should become part of the specification of every genotype. Given this information, it would be easier to help farmers choose the correct crop cultivar and management practices for any new climatic conditions.

**Technical Abstract:** The gradual accumulation of carbon dioxide and other gases in the atmosphere is expected to cause climate change. This will result in combinations of soil, climate and carbon dioxide concentration [CO<sub>2</sub>] that have not been experienced previously. Crop models are the only realistic tools available for predicting how yields might change. Since the models will be used to extrapolate beyond the range of existing databases they must be mechanistic. They must also mimic crop responses to a wide range of temperatures and to [CO<sub>2</sub>], especially the long-term response of stomata to elevated [CO<sub>2</sub>] and the resulting water use by the crop. However, even with adequate models it is not enough to predict crop yields assuming that everything except weather and [CO<sub>2</sub>] will remain the same. Farmers and agronomists have a long record of adapting crop ecosystems to changing conditions. In some locations, climate change will lengthen the growing season; in others it will shorten the season by virtue of high summer temperatures or drought. More fertilizer will be needed to take full advantage of increased photosynthesis in high [CO<sub>2</sub>]. The farmer will respond by changing planting date, planting density, fertilizer application rate, cultivar and even species. Predictions of crop yield in a future climate must assume that the producer will optimize his management practices for the new environment.

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## MODELING SOLUBLE CHEMICAL TRANSFER FROM SOIL TO OVERLAND FLOW AND ITS TRANSPORT THROUGH MACROPORES TO GROUNDWATER

AHUJA L R, TIMLIN D J, HEATHMAN G C

**Interpretive Summary:** The transport of nutrients and pesticides in runoff is both an economic loss and a threat to the quality of our surface waters. Recent studies indicate that a part of this so-called runoff, containing the chemicals, enters the soil macropore channels open at the surface, which rapidly transport the solution to groundwater. The practice of minimum or no tillage exacerbates this problem, by enhancing worm activity and allowing macropore channels to stay open, and by greater pesticide use and their application on the soil surface. In this paper, we quantify the process of chemical transfer to runoff and its transport through macropores. We then use the model to show that the chemical transport through macropores depends greatly on the rainfall intensity and amount, flow capacity of macropores, and the type of chemical. The model can, thus, help in designing management practices that will minimize the transport in different areas.

**Technical Abstract:** Theoretically based methodologies for modeling soluble chemical transport from soil to overland flow and subsequent transfer to soil macropores are developed. Chemical transfer to overland flow is best modeled as an accelerated diffusion process driven by raindrop impact. A simplified non-uniform mixing model which allows an exponentially decreasing contribution of chemical to overland flow with depth is a good approximation to above. Predicted chemical transfer to overland flow compares well with experimental data. Transfer of water and solutes to soil from macropore flow utilizes a physically based Green-Ampt approach to compute radial infiltration into the soil matrix. Macropores greatly increase simulated infiltration. The total amount of chemical transported is more strongly influenced by the total flow capacity of macropores and rainfall rather than the sizes of the macropores. More of a moderately adsorbed chemical is transported through macropores.

Submitted to: (approved 02/15/91) INTERNATIONAL MEETING

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## BASIC SOIL FERTILITY PRINCIPLES

BANDEL VERNON A, JAMES BRUCE R, MEISINGER JOHN J

**Interpretive Summary:** Farmers need to know about basic soil fertility in order to manage nutrients for farm profitability and to maintain the quality of our environment. This extension service bulletin reviews the sources of nutrients, transformation and fate of nutrients, and the plant availability of the 13 essential nutrients. These 13 nutrients consist of the primary nutrients nitrogen, phosphorus and potassium; the secondary nutrients of calcium, magnesium and sulfur; and the micro nutrients of copper, zinc, manganese, boron, iron, molybdenum, and chloride. The importance of soil pH, soil organic matter, soil cation exchange capacity, and soil texture are also discussed. The plant availability of these nutrients is assessed through soil tests which are the best way to inventory a farms' soil resources on a regular basis. Understanding basic soil fertility will help farmers improve nutrient use efficiencies in Maryland and should reduce nutrient losses to Chesapeake Bay.

**Technical Abstract:** Managing soil fertility is essential for profitable agriculture and to maintain our environment. This bulletin reviews basic soil fertility principles for the 3 primary nutrients (N, P and K), the 3 secondary nutrients (Ca, Mg and S) and the 7 micronutrient (Cu, Mn, Zn, B, Fe, Mo and Cl) including their transformations in soil and their plant availability as related to soil Ph, soil organic matter, soil texture, soil cation exchange capacity (CEC) and soil aeration. The soil testing procedures for these 13 nutrients are reviewed, as well as the testing procedures for pH, organic matter, CEC, and texture. Soil tests must be calibrated against actual crop response in the field before a fertilizer recommendation can be made. It is important for modern farmers to inventory their soil resources through regular soil testing and to wisely use manures and fertilizers as nutrient resources. This publication will help train farmers and extension service personnel to improve nutrient use efficiencies in Maryland and should reduce nutrient losses to the environment.

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## A PROPOSED DESCRIPTION OF SOIL POROSITY

BRAKENSIEK DONALD L, RAWLS WALTER J, LOGSDON S D, EDWARDS W

**Interpretive Summary:** The size and number of soil pores are critical to movement of soil water and chemicals. A statistical technique was developed for describing the pore size distribution. The pore size distribution function changes with management and allows the water flow process to be evaluated for management effects.

**Technical Abstract:** Quantifying soil porosity by pore size and numbers has been identified as an important need in soil water hydrology and hydrologic computations. Proposed classification of soil porosity based primarily by pore size have essentially been rejected. How to accomplish this and provide input to the dynamic process of channeling flows is still being discussed. The self-similar scaling property of fractals has the potential for a continuum description of soil porosity. We have used field collected soil pore size data to evaluate the utility of fractal geometry for quantifying soil pore size distributions and aerial porosity over several cycles of pore radii. Statistical evidence is presented to suggest that the Sierpinski carpet can be used as an algorithm to compute soil pore size and numbers and aerial porosity. Parameters of pore size distribution function can possibly be related to soil management porosity.

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## NITROGEN REQUIREMENTS FOR CORN

BUNDY LARRY G, BANDEL VERNON A, MEISINGER JOHN J

**Interpretive Summary:** It is essential to make accurate corn fertilizer nitrogen (N) recommendations in order to ensure farm profitability and to minimize environmental concerns. Corn takes up N from fertilizers, manure, previous legume crops, residual nitrate, and soil organic matter-so all sources of N must be considered in order to manage N efficiently. Corn fertilizer N needs should first consider the N required by the crop. This is usually figured from the expected yield or yield goal, which can be calculated from the 3-5 year average yields for a field. A factor of 1.2 lb N/bu is then multiplied by the expected yield to estimate the crop N need, but recent research suggests that 1.0 lb N/bu is more appropriate in several states. The non-fertilizer N sources of a site must also be taken into account in order to optimize N recommendations, these include: manure applications, previous legume crops, soil organic matter, and residual nitrate. These can be assessed through manure tests, cropping histories, fertilizer replacement credits, and soil nitrate tests. It is not unusual to have manure or recent forage legume residues furnish most of the corn N requirement. Preplant and pre-sidedress soil nitrate tests also have great potential for improving the accuracy of corn fertilizer N recommendations. Adjustments for non-fertilizer N sources must be subtracted from the base corn N requirement. Field soil N test calibration programs should continue to refine and improve corn N recommendations so that profitable corn production is achieved and environmental effects are minimized.

**Technical Abstract:** A summary was made of methods used to determine corn fertilizer N (FN) requirements. Accurate FN recommendations are essential for profitable corn production and for minimizing adverse environmental effects. Corn utilizes N from fertilizers, manure, previous legume crops, residual NO<sub>3</sub>-N and soil organic matter; which emphasizes the need to manage all sources of N efficiently. Estimating the corn FN requirement first involves site-specific assessment of the N required by the crop; which is commonly based on expected yield or yield goals although other approaches are also in use. A conversion factor of 1.2 lb N bu<sup>-1</sup> of expected grain yield is widely used, but recent research suggests that 1.0 lb N bu<sup>-1</sup> is more appropriate in several states. Realistic yield goals are essential and are best estimated using 3-5 year averages of actual yields from a field. The non-FN inputs of a site must also be taken into account in order to optimize FN recommendations, these include: manure applications, previous legume crops, soil organic matter, and residual NO<sub>3</sub>-N. These can be assessed through manure tests, cropping histories, fertilizer replacement credits, and soil nitrate tests. It is not unusual to have manure or recent forage legume residues furnish all, or a major portion of, the corn N requirement. Preplant and pre-sidedress soil NO<sub>3</sub>-N tests have great potential for improving the accuracy of FN contributions from the corn N requirement, the adjustments for non-FN sources must be made on site-specific information. Alternatively, FN recommendations can be based on N response data from representative soils. Field N test calibration programs with NO<sub>3</sub>-N monitoring should produce FN recommendation systems that give profitable corn production and minimize environmental effects.

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## LEGUME COVER CROP CONTRIBUTIONS TO NO-TILLAGE CORN PRODUCTION SYSTEMS

DECKER A M, CLARK A J, MEISINGER J J, MULFORD R F, MCINTOSH M S

**Interpretive Summary:** Farmers and farm advisors need information on optimum fertilizer nitrogen levels for corn following winter covers because covers can supply nitrogen and conserve moisture for the next crop. Research in the Coastal Plain and Piedmont regions of Maryland evaluated fertilizer nitrogen rates and winter cover crops of hairy vetch, Austrian winter pea, crimson clover, and wheat on no-tillage corn production. Cover crop dry matter and N content were measured, as well as corn N uptake, grain yield and silage yield. Cover crop N contents (in lb N/acre) in the Coastal Plain averaged about 185 for hairy vetch, 160 for peas, 150 for crimson clover, and 35 for wheat. Corresponding values in the Piedmont were about 40% lower due to shorter winter growing seasons. With no fertilizer nitrogen corn grain yields were higher following legume covers than after no-cover and were lowest following wheat. Corn grain yields were about 10-15% greater after fertilized legume covers than after a fertilized wheat cover or no-cover. More efficient conservation of summer moisture was the likely reason for this added yield. The fertilizer nitrogen needs without a cover crop averaged about 120 and 65 lb N/acre in the Coastal Plain and Piedmont regions, respectively. With a grass cover crop the average fertilizer nitrogen need increased about 10-25 lb N/acre, while after a legume cover it decreased about 20-65 lb N/acre. These results will be very useful to farmers and farm advisors because they demonstrate the nitrogen supplying ability and water conservation benefits of winter cover crops. This information should speed the adoption of winter cover cropping into modern conservation tillage cropping systems.

**Technical Abstract:** Winter cover crops can supply nitrogen (N) and conserve moisture for the next crop. Data are needed on optimum fertilizer N (FN) levels for summer crops following winter covers. A three-year study was conducted in the Coastal Plain and Piedmont regions of Maryland to evaluate the effect of winter cover crops of hairy vetch (*Vicia villosa* Roth), Austrian winter pea (*Pisum sativa* (L) Poir), crimson clover (*Trifolium incarnatum* L.) and wheat (*Triticum aestivum* L.) on no-tillage corn (*Zea mays* L.) production. These studies evaluated cover crops and four FN rates. Crop parameters studied were: cover crop N content, corn N uptake, and corn grain and silage yields. Nitrogen contained in the Coastal Plain cover crops averaged about 205, 180, 170, and 40 kg N ha<sup>-1</sup> for hairy vetch, peas, crimson clover, and wheat; respectively. Corresponding Piedmont values were about 40% lower due to a shorter growing season. With no FN corn grain yields were higher following legume covers than after no-cover and were lowest following wheat. There was a synergistic response between legume cover crops and FN, especially with hairy vetch, with the greatest corn yields occurring after legumes fertilized with 90-135 kg N ha<sup>-1</sup>. More efficient summer water utilization was the likely reason for this synergism. Because of the difference in maximum yields the FN needed to achieve optimum yields was not related to cover crop N content. The FN needs without a cover crop averaged about 75 kg N ha<sup>-1</sup> in the Piedmont and about 135 kg N ha<sup>-1</sup> in the Coastal Plains. Greater efforts should be made to incorporate winter cover crops into modern cropping systems.

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## PHOTOSYNTHATE METABOLISM IN THE SOURCE LEAVES OF N<sub>2</sub>-FIXING SOYBEAN PLANTS

DE VEAU EDWARD J, ROBINSON J M, WARMBRODT R D, KREMER DIANE F

**Interpretive Summary:** A problem of national magnitude has been the extreme overuse of nitrate and ammonia fertilizers in the farms of North America. In many parts of the U.S., nitrates severely contaminate ground water supplies, and alternatives are sought to limit the use of nitrogen fertilizers. Leguminous plants such as soybean are able to unite symbiotically with N<sub>2</sub>-fixing bacteria. If the symbiosis is effective, the bacteria provide most or all of the ammonia needed by that plant, and there is no need to use nitrogen fertilizers. However, conditions in the farm field sometimes preclude an effective symbiosis between the host plant soybean, and its symbiont, root nodule, bacteria, *Bradyrhizobium japonicum*. A way to determine the effectiveness of the symbiosis by examination of the plant leaves is needed. This work reports that soybean leaf synthesis of carbohydrates such as starch is a measure of the effectiveness of the symbiotic relationship. The work is leading toward the ability of farmers and grower groups to assess the need to supply additional nitrate and ammonia fertilizer to the nitrogen-fixing soybean plant by monitoring the leaf carbohydrate status.

**Technical Abstract:** *Glycine max* [L.] Merr. cv Williams plants, which were symbiotic with *Bradyrhizobium japonicum*, and which acquired reduced nitrogen solely through N<sub>2</sub> fixation processes (N<sub>2</sub>Fx plants), often exhibited excess accumulation of starch and sucrose in their source leaves when compared with counterpart soybean plants which had been supplied from emergence with growth sufficient levels of inorganic nitrogen (6 mM NO<sub>3</sub><sup>-</sup>/6 mM NH<sub>4</sub><sup>+</sup>)(NS plants). Since there was a minimal requirement for carbon skeletons to support amino acid synthesis, enhanced foliar starch accumulation appeared to be related to a considerable excess of hexose phosphates generated during CO<sub>2</sub> assimilation. Evidence suggested that increased starch accumulation in N<sub>2</sub>Fx plants was facilitated by: 1) an adaptive increase of activities of several enzymes of the chloroplast starch synthesis pathway including, fructose-1,6-bisphosphate(C-1) phosphatase, phosphohexoisomerase, phosphoglucumutase and adenosine diphosphate glucose pyrophosphorylase (ADPG-PPiase) (in some leaves), and 2) increased foliar levels of hexose monophosphates, e.g. fructose-6-phosphate, glucose-6-phosphate, and glucose-1-phosphate (G-1-P) which apparently had risen to levels considerably in excess of the K<sub>m</sub>s for their respective target enzymes, e.g. G-1-P with respect to ADPG-PPiase.

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# ROLE OF EARTHWORM MACROPORES FORMED BY APPECTODEA TUBERCULATA ON PREFERENTIAL FLOW OF WATER THROUGH A TYPIC HAPLUDOLL

ELA STEVE D, GUPTA SATISH C, RAWLS WALTER J, MONCRIEF JOHN F

**Interpretive Summary:** Macropores are a major conductor of water and contaminants. Understanding the role of the biological factors is critical to identify the pathways. A laboratory study identified that number and size of earthworms macropores are insufficient to describe infiltration thus, more information such as connectivity, and biological coatings need to be integrated into the macropore description.

**Technical Abstract:** Aporectodea spp. earthworms are the most dominating earthworms in cultivated soils of the north central region. A laboratory experiment examined the role of macropores formed by Aporectodea spp. on water infiltration into two Minnesota soils. The experiment consisted of incubating soil containers with seven Aporectodea spp. earthworms for six weeks and then subjecting the soil surface to artificial rainfall impact. Infiltration was measured from the increase in container weight over time. Treatments included two rainfall intensities (9 and 30 mm s<sup>-1</sup>), presence and absence of surface cover, and presence and absence of earthworms macropores. After the rainfall infiltration rates with a disk parameter at three tensions and several depths were also measured to examine the continuity of macropores with soil depth and to calculate the contribution of macro- and meso-pore fluxes. Comparisons of rain infiltration rates on bare and covered soils showed that development of surface seal on the bare soil was effective in sealing the visible macropores varying in diameter from 2 to 5 mm. In addition, macropores were ineffective in conducting water because they were unconnected to the subsurface macropores. This was mostly due to blockage of macropores by castings and in some cases due to the blockage by earthworms. Both the infiltration rate at 0 mm tension and macropore flux were unrelated to the number of visible macropores or macropore size.

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## PREDICTING N FERTILIZER NEEDS FOR CORN IN HUMID REGIONS: ADVANCES IN THE MID-ATLANTIC STATES

FOX RICHARD M, MEISINGER JOHN J, SIMS THOMAS, PIEKIELEK W P

**Interpretive Summary:** Residents of the Mid-Atlantic region are concerned about nitrate pollution of groundwater and the Chesapeake Bay. Agricultural researchers in Pennsylvania, Maryland, and Delaware have evaluated 221 field trials which investigated the applicability of a soil nitrate test for corn which should reduce nitrate leaching from agriculture. The test measures the nitrate concentration in the top foot of soil when the corn is about 12 inches tall, which is about two weeks before normal sidedress fertilizer nitrogen is applied. In 82% of the cases the test successfully identified nitrogen sufficient sites, that is, identified sites which need no additional fertilizer. The accuracy of the test was not affected by tillage practices. The nitrate test is most useful for manured fields where uncertainties in application rates and N losses make nitrogen management very difficult. This test will help extension agents, nutrient management consultants, and farmers identify nitrogen sufficient sites and thereby conserve fertilizer nitrogen and reduce nitrate losses to groundwater and the Chesapeake Bay.

**Technical Abstract:** Improving nitrogen fertilizer use efficiency is an important task for agricultural scientists, because it will ensure that farmers are able to supply ample nitrogen (N) to meet crop demands yet avoid excessive N applications that could cause nitrate pollution of groundwater or the Chesapeake Bay. The pre-sidedress nitrate test (PSNT) is one tool to improve N fertilizer use efficiency; it measures the soil  $\text{NO}_3\text{-N}$  concentration in the surface 30 cm of soil when the corn plants are 30 cm tall. A combined analysis of PSNT data from 221 field trials in Pennsylvania, Maryland, and Delaware was conducted to evaluate the overall usefulness of the PSNT as a predictor of fertilizer N response. The evaluation showed that PSNT as a predictor of fertilizer N response. The evaluation showed that PSNT values greater than 22 mg N  $\text{kg}^{-1}$  were associated with N sufficiency. The PSNT was a good predictor of N sufficiency, with non-responding sites correctly identified 82% of the time. However, the PSNT was not a good predictor of relative grain yields for sites with less than 22 mg N  $\text{kg}^{-1}$ , especially if the site was first-year corn after a forage legume. The PSNT seems to be best suited for manured fields where uncertainties in manure loading rates and N losses due to ammonia volatilization and denitrification are highly variable. Tillage practice has little or no effect on the PSNT accuracy. Use of the PSNT should reduce the practice of applying "insurance N" which should improve fertilizer N use efficiency and reduce  $\text{NO}_3\text{-N}$  contamination of our water resources.

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## MODELING PREFERENTIAL MOVEMENT OF AGRICULTURAL CHEMICALS

GISH TIMOTHY J  
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**Interpretive Summary:** For the past decade there has been a great deal of public and political concern over the impact of agriculture on the environment. This concern has lead to a need for mathematical models having the ability to quantify agricultural chemical behavior in soil. However, the lack of adequate field data has made it impossible to quantify field-scale transport processes, so the assumptions inherent in laboratory studies have been extended to the field. Unfortunately, the fluid dynamics of a laboratory soil column are much different than a non-homogeneous field soil. Consequently, laboratory results have shown to be a poor indicator of field-scale movement of agricultural chemicals. Recent field-scale research is beginning to show which chemical transport processes are important on a large scale. This manuscript uses the observed results to determine a more realistic derivation of a field-scale chemical transport model.

**Technical Abstract:** The classical convection-dispersion equation (CDE) has proven to be inadequate in simulating field-scale behavior. Part of the failure in field-scale models using the CDE is that detailed information about chemical behavior is sacrificed so as to account for other chemical and biological processes. Unfortunately, little is known concerning which process can be sacrificed without significantly effecting simulation results. Consequently, field-data from two recently conducted experiments was used to evaluate the classical CDE. Results indicate that simulation of field-scale chemical non-equilibrium, and no-homogenous flow regime may be drastically improved by using a two site mobile-immobile representation with two dissipation and adsorption parameters. The adsorption and dissipation coefficients are partitioned between the inter and intra-aggregate pore space.

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## FIELD-SCALE MOBILITY AND PERSISTENCE OF COMMERCIAL AND STARCH-ENCAPSULATED ATRAZINE AND ALACHLOR

GISH TIMOTHY J, SHIRMOHAMMADI, A, WIENHOLD B

**Interpretive Summary:** Atrazine and alachlor are two of the most widely used herbicides in modern agriculture. Unfortunately, these two herbicides are two of the most frequently observed herbicides in groundwater. To address these problems, the Agricultural Research Service has been investigating various herbicide formulations that could effect environmental impact. One developing technology involves encapsulating the herbicide not with a membrane coating, but encapsulating the pesticide in such a way that it is dispersed throughout the granule. This manuscript reports on a two-year field study showing that starch-encapsulation reduces herbicide mobility when compared to commercial formulations. By decreasing leachate losses, herbicide soil persistence increased.

**Technical Abstract:** Recent laboratory and small field plot studies have shown that starch-encapsulation (SE) may reduce both volatilization and leachate losses of certain pesticides relative to commercial formulation (CF). This study compares field-scale mobility and persistence of atrazine [2-chloro-4-ethylamino-6-isopropylamino-s-triazine] and alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide] in both SE and CF. The field site consists of four unreplicated watersheds, approximately 0.2 ha each. Two watersheds were under no-till management; one receiving atrazine and alachlor in the SE formulation and the other receiving the herbicides in CF. The remaining two fields were under conventional tillage; one receiving SE and the other CF. Chemical movement and persistence was determined by analysis of 1.1 m soil cores for herbicides. The significantly increased persistence of SE-atrazine relative to CF-atrazine was attributed to the reduction of leachate losses. This decrease in mobility may be an indication of atrazine diffusion into the soil matrix, where it is less subject to preferential flow processes. Alachlor residue levels 1 h and 12 d post-application were significantly larger for the SE formulation than for either of the two CF formulations. This difference at early times is attributed to SE causing reduced alachlor loss during application. Unlike with atrazine, alachlor mobility was not dramatically reduced by the SE formulation.

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## EFFECT OF STARCH-ENCAPSULATION ON BEHAVIOR OF ATRAZINE AND ALACHLOR

GISH TIMOTHY J, WIENHOLD B, SHIRMOHAMMADI A

**Interpretive Summary:** Atrazine and alachlor are among two of the most widely used herbicides which have been frequently detected as contaminants in groundwater and in the atmosphere. As a result, USDA-ARS has been evaluating agricultural alternatives that will minimize the impact of these herbicides on the environment. Starch-encapsulation is an alternative to the present commercial formulations that modifies how the herbicides interacts with the soil environment. This manuscript discusses recent laboratory, greenhouse, and field experiments that evaluate how starch-encapsulation modifies environmental impact relative to presently available commercial formulations.

**Technical Abstract:** To maintain high agricultural yields, large quantities of herbicides are applied to soils each year. After application, these herbicides can impact the environment via leaching to groundwater, volatilization, and surface transport through runoff and soil erosion. The purpose of this paper is to review recent work with a developing technology, starch-encapsulation (SE). Starch-encapsulation allows for reproducible herbicide release rates from starch granules. By controlling the rate of release, herbicide behavior can be modified. The magnitude of the modification is variable, dependent on chemical characteristics of the encapsulated herbicide, granule characteristics, and the soil-water environment. Starch encapsulation has been shown to reduce cumulative volatilization losses of atrazine; reduce runoff losses of atrazine and alachlor; reduce leaching of surface applied atrazine; and increase persistence of atrazine. These results suggest that SE may be a viable way of reducing detrimental environmental affects associated with the use of agricultural pesticides.

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## ATRAZINE RELEASE FROM STARCH-ENCAPSULATED FORMULATIONS AND PERSISTENCE IN SOIL

GISH TJ, SCHREIBER MM, SCHOPPET MJ, WEINHOLD BJ, HELLING CS, WING RE

**Interpretive Summary:** Previously, the rapid movement of atrazine was severely retarded by the use of starch-encapsulated formulations. However, the environmental fate of pesticides is a combination of mobility and persistence. Pesticide release and persistence in soil is a function of a number of soil and climatic factors. This study was conducted to evaluate the impact of several of these factors on the release and persistence of atrazine from newly developed ARS starch-encapsulated formulations. Results indicate that one of the new starch encapsulated process (jet-cooking) increases atrazine persistence in soil. As a result, field-scale interaction between surface and subsurface hydrology will be critical in determining the applicability of this formulations in agriculture.

**Technical Abstract:** Atrazine release as a function of water potential, and atrazine persistence rates in soil, were evaluated for three starch-encapsulated formulations. Capsule swelling and atrazine release rates from borate, jet-cooked pearl, and jet cooked waxy formulations were evaluated at several water potentials from 0.0 to -1.5 MPa. Rate of atrazine release as well as the maximum equilibrium solution concentration of the herbicide decreased with decreasing water potential. Relative to published field observations, atrazine persistence in this laboratory study was lower due to high soil moisture conditions, high organic matter content, and slightly higher temperatures. Persistence rates were greatest for the jet-cooked encapsulated atrazine and shortest for technical grade. Enhanced atrazine persistence associated with encapsulation appears to be a short-term phenomenon, inversely related to the biodegradability of the starch matrix. Nomenclature: Atrazine, (6-chloro-N<sup>H</sup>-ethyl-N<sup>H</sup>-(1-methylethyl)-1,3,5-triazine-2,4-diamine).

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## THE EFFECT OF INOCULANT STRAIN AND ORGANIC MATTER CONTENT ON THE KINETICS OF 2,4-DICHLOROPHENOXYACID DEGRADATION IN SOIL

GREER LINDA E, SHELTON DANIEL R

**Interpretive Summary:** Soil bioremediation involves the use of microorganisms to detoxify and degrade pollutants in soil. In order for soil bioremediation to be successful, it is necessary that the appropriate strains be present or for the appropriate strains to be added to the soil (inoculation). In addition, it is critical that the microorganisms be able to survive and reproduce in the soil, and be able to degrade the pollutant at whatever concentration it may be present. In this study, the effect of choosing inoculant strains with different affinities for the herbicide 2,4-D on the rate of 2,4-D degradation in soil were examined. It was observed that at higher 2,4-D concentrations rates of degradation were comparable for two different strains, however, at lower concentrations the strain with the greater affinity for 2,4-D in liquid culture also degraded the 2,4-D faster and to a greater extent in soil. These results suggest that the choice of inoculant strain may be of considerable importance depending on the concentration of pollutant in soil. The effect of soil organic matter on rates of degradation were also investigated, since organic matter tends to adsorb pollutants, making them less available to microorganisms. As expected, rates of 2,4-D degradation in soils with high organic matter were slower than in soils with low organic matter using the same inoculant strain. These data demonstrate the importance of taking into consideration soil characteristics and pollutant concentrations when selecting an inoculant strain and in predicting rates of pollutant degradation.

**Technical Abstract:** Rates of degradation of soluble and sorbed 2,4-D were monitored in low organic matter soil at field capacity amended with 1, 10, or 100 ug 2,4-D/g wet soil and inoculated with one of two bacterial strains (MI, 155) with similar maximum growth rates ( $U_{max}$ ) but significantly different half saturation growth constants ( $K_s$ ). Concentrations of soluble 2,4-D were determined by analyzing samples of pore water pressed from soil while sorbed 2,4-D was determined by solvent extraction. Sixty-five to seventy-five percent of total 2,4-D was present in the soluble phase at equilibrium, resulting in soil solution concentrations of ca. 8, 60, and 600 ug/ml 2,4-D, respectively. Soluble 2,4-D was metabolized preferentially, followed by degradation of both sorbed (after desorption) and soluble 2,4-D. Rates of degradation were comparable for both strains at soil concentrations of 10 and 100 ug/g 2,4-D, however, at 1 ug/g soil, 2,4-D was metabolized more rapidly by the strain with the lower  $K_s$  value (MI). Rates of biodegradation of soluble and sorbed 2,4-D were also monitored in high organic matter soil at field capacity amended with 100 ug 2,4-D/g wet soil and inoculated with the low  $K_s$  strain (MI). Ten percent of total 2,4-D was present in the soluble phase, resulting in a soil solution concentration of ca. 30 ug/ml 2,4-D. Rates of degradation in the high organic matter soil were slower than in the low organic matter soil, presumably, due to slower rates of desorption and microbial growth.

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## PHYSIOLOGICAL AND KINETIC COMPARISON OF SEVEN STRAINS OF 2,4-DICHLOROPHENOXYACETIC ACID DEGRADING BACTERIA

GREER LINDA E, ROBINSON JOSEPH A, SHELTON DANIEL R

**Interpretive Summary:** Bioremediation is the process by which microorganisms are used to detoxify and/or degrade wastes and pollutants in the environment. In some instances the appropriate microorganisms may already be present at the site but in others it may be necessary to add or inoculate the site with the appropriate strains. In such situations it is necessary to select inoculant strains which will be able to survive and reproduce at the contaminated site, frequently under adverse environmental conditions. This requires that numerous pollutant degrading microorganisms be isolated and studied in order to develop a library of strains possessing a variety of different physiological and kinetic characteristics. Depending on the environmental characteristics of the site to be remediated, the most appropriate strain(s) can be selected for inoculation at that site. This study involves the isolation and characterization of several different strains of bacteria able to degrade the commonly used herbicide, 2,4-D, each with one or more unique characteristics which may be important in allowing that strain to survive and reproduce at a given site. This study demonstrates that diversity is common among naturally occurring microorganisms and that it should be possible to develop libraries of such pollutant degrading strains.

**Technical Abstract:** Seven strains of 2,4-dichlorophenoxyacetic acid-degrading bacteria, including species of *Pseudomonas*, *Alcaligenes* and *Bordetella*, were compared on the basis of substrate range, mortality, and growth kinetics. Estimates of maximum growth rate ( $U_{max}$ ,  $k_1$ ) and half saturation growth constant ( $K_s$ ,  $k_3$ ) were obtained by fitting substrate depletion curves to a four parameter version of the integrated Monod equation. Estimates of  $K_s$  ranged from 2.2 ug/ml (10 uM) to 33.8 ug/ml (154 uM), while estimates of  $U_{max}$  ranged from 0.20 hr<sup>-1</sup> ( $T_d$  = 3.5 hr) to 0.32 hr<sup>-1</sup> ( $T_d$  = 2.2 hr). Estimates of  $U_{max}$ , but not  $K_s$ , were affected by changes in initial inoculum density. Maximum growth rates ( $U_{max}$ ) were also estimated from turbidity measurements. Estimates of  $U_{max}$  ranged from 0.10 hr<sup>-1</sup> ( $T_d$  = 6.9 hr) to 1.0 hr<sup>-1</sup> ( $T_d$  = 0.7 hr). There was no correlation between estimates of  $U_{max}$  derived from substrate depletion curves and turbidity measurements ( $P=0.20$ ). Mortality rates (27 C) varied dramatically between strains, with losses ranging from 90% in 28 days to greater than 4 orders of magnitude in 15 days. There was considerable variation in the ability of the seven strains to use different monomeric and polymeric carbon sources as growth substrates. Data from this study demonstrate there is significant physiological and kinetic variation in parameters likely to affect the survival and proliferation of 2,4-D degrading bacteria in the environment.

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## EXPRESSION OF ACHROMOBACTER CARBOFURAN HYDROLASE IN ESCHERICHIA COLI

HAUSCHILD J E, FRIED S G, KARNS J S, TOMASEK P H

**Interpretive Summary:** Carbofuran hydrolase is an enzyme that can inactivate many methylcarbamate insecticides, including carbofuran, carbaryl, and aldicarb. This enzyme was identified in the soil bacterium *Achromobacter* species WM111 and the gene encoding it (the *mcd* gene) was cloned. WM111 is a slow growing bacterium with no known mechanisms for genetic manipulation so using strains containing the cloned gene for further study of the gene or enzyme would be very convenient. However, the amount of active carbofuran hydrolase produced in strains of bacteria containing the cloned *mcd* gene was very low. In this study it was shown that the reason for the low amount of enzyme activity in strains of *E. coli* carrying the cloned *mcd* gene was that the bulk of the protein produced was incorporated into insoluble inclusion bodies. Reduction of the temperature at which the cells were grown from 37 to 30 degrees centigrade resulted in a higher percentage of the carbofuran hydrolase protein synthesized in its active form such that more activity was obtained at 30 degrees even though the total amount of carbofuran hydrolase protein produced was less. The orientation of the gene on the cloned DNA fragment was also established. These results will aid in efforts to produce large amount of carbofuran hydrolase for use in studies on removal of carbamate insecticides from the environment.

**Technical Abstract:** Carbofuran hydrolase from *Achromobacter* sp. strain WM111 is encoded by the plasmid-borne *mcd* gene. This enzyme hydrolyzes N-methylcarbamate pesticides yielding methylamine which can then be utilized as a nitrogen source by strain WM111. A 3.1 kilobase-pair (kb) *Cla* I-*Cla* I DNA fragment containing the *mcd* gene was cloned into the pBlueScript SKII+ vector and introduced into *E. coli*. *E. coli* clones producing carbofuran hydrolase were identified using a carbaryl/fast blue RR plate assay. Only one orientation of the cloned insert demonstrated carbofuran hydrolase activity by this assay, establishing the direction of *mcd* transcription. Using a *xylE* promoter probe vector, the region upstream of the *mcd* structural gene was shown to contain a promoter which functioned poorly in *E. coli*. Deletion of approximately 500 base pairs from the 3.1 *Cla* I fragment in the region 5' to the *mcd* structural gene resulted in a two to four fold increase in the level of carbofuran hydrolase activity in *E. coli*. This increased expression of the gene resulted in the formation of inclusion bodies which limited the amount of active enzyme that could be obtained from cells grown at 37 degrees centigrade. Reduction of the growth temperature to 30 degrees reduced inclusion body formation such that a higher proportion of the enzyme was produced in its active form.

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## TWO POLYPEPTIDES ASSOCIATED WITH ACHROMOBACTER CARBOFURAN HYDROLASE INTERACT TO PRODUCE THREE ACTIVE FORMS OF THE DIMERIC ENZYME

HAUSCHILD J E, KARNS J S, TOMASEK P H

**Interpretive Summary:** The soil bacterium *Achromobacter* sp. strain WM111 produces an active carbofuran hydrolase that cleaves the N-methylcarbamate linkage of many insecticides including carbofuran, carbaryl, and aldicarb. When this enzyme was purified it was seen that the enzyme was made up of 2 polypeptide subunits, 1 of 72 kilodaltons (kDa) in size and the other of 77 kDa. When the *mcd* gene encoding carbofuran hydrolase was cloned into *Pseudomonas putida* it was shown that the gene resided on a 3 kilobase (kb) DNA fragment and that both the 72 and 77 kDa polypeptides were produced. This is unusual because a 3 kb DNA fragment cannot code for two polypeptides of this size (2 kb of DNA encodes a polypeptide of about 77 kDa) unless the genes share substantial overlap. This study shows that the two polypeptides are, for the most part, identical. Thus, we conclude that either the 72 kDa peptide is derived from the 77 kDa peptide by proteolytic cleavage or that there are two translation start sites on the messenger RNA transcribed from the *mcd* gene such that different sized peptides are made from the same in-frame reading of the *mcd* message. The two polypeptides can combine in all possible combinations to form 3 different sizes of the carbofuran hydrolase enzyme, all of which have activity. Two different translation start sites for one enzyme may mean that this soil bacterium has a means of regulating enzyme synthesis at the level of translation.

**Technical Abstract:** *Achromobacter* sp. strain WM111 is a soil bacterium which produces the enzyme carbofuran hydrolase. In addition to carbofuran, carbofuran hydrolase hydrolyzes other N-methylcarbamate pesticides such as carbaryl and aldicarb, allowing these compounds to be utilized as the organism's sole nitrogen source. The molecular mass of native carbofuran hydrolase is approximately 150 kilodaltons (kDa). SDS-polyacrylamide gel electrophoresis of purified carbofuran hydrolase shows the presence of two polypeptide subunits with masses of 72 and 77 kDa. Three forms of the active carbofuran hydrolase dimer were identified on native polyacrylamide gels stained for activity. These bands were excised from the gels and run on SDS denaturing polyacrylamide gels to determine the subunit associations in the three active carbofuran hydrolase holoenzymes. The three forms of the active enzyme were formed from the dimerization of all possible combinations of the two polypeptide subunits. Protease digestion of the gel purified polypeptides demonstrated that the two protein subunits were essentially identical.

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## PHYSICAL AND CHEMICAL PROCESSES AFFECTING PREFERENTIAL FLOW

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GISH TIMOTHY J

**Interpretive Summary:** Evidence has mounted over the past 10-20 years linking deeper than expected leaching of some agrichemicals into soils with preferred flow pathways. One major type includes macropores - large pores, fissures, channels, or other semi-continuous voids. These may be caused biologically, following decay of roots or through burrowing of earthworms or arthropods.

Alternatively, macropores may form by natural soil aggregation. Fingering of soil water is a type of preferential flow caused by wetting front instability, and is most likely to occur in coarse-textured soils, especially at textural discontinuities. Nitrate, dye tracers, and pesticides of intermediate mobility have been shown to leach preferentially. For pesticides, transport through macropores is most likely when moderate to heavy rainfall occurs soon after application. Preferential flow appears to be more likely under long-term no-till conditions than with conventional till.

**Technical Abstract:** Over the past 10-20 years evidence has mounted linking deeper than expected leaching of some agrichemicals into soils with preferred flow pathways. One major type includes macropores - large pores, fissures, channels, or other semi-continuous voids. These may be caused biologically, following decay of roots or through burrowing of earthworms or arthropods.

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## SIMULTANEOUS NONLINEAR IRREVERSIBLE REACTION AND MOVEMENT OF SOLUTES IN SOILS

HOGARTH W L, PARLANGE J Y, STARR J L

**Interpretive Summary:** The ability to model the simultaneous irreversible reaction and movement of nitrates and other agrochemicals in soils is important in environmental studies. This paper presents a new mathematical model for a two-substrate reaction and movement, e.g., nitrate-N and glucose-C, that enables the full range of kinetics to be explored. The model provided excellent characterization of nitrate outflow concentrations from laboratory column studies. This model will provide a more accurate mathematical tool to environmental scientists to provide initial estimates of natural reaction rate coefficients; comparison of these values under different environmental conditions; and estimates of microbially induced effects on the movement of nitrates to groundwater.

**Technical Abstract:** This paper presents an approximate analytical solution for a nonlinear irreversible reaction involving the movement of solute when two substrates are involved. The presence of the second substrate determines when the reaction will proceed. The implicit solution obtained enables the continuum of irreversible reactions to be explored through the Michaelis-Menten form. The effect of the second substrate being present or not at the start of the reaction is investigated. Validation of the approximate analytical solution is achieved by systematic comparison with a numerical solution. The effect of boundary conditions on the solution for a finite column is examined. With a change from aerobic to anaerobic conditions initially, the effect on the breakthrough curves and concentration profiles of having a flux-concentration inlet boundary condition with a zero-flux outlet condition for a finite column is compared with a fixed-concentration inlet condition for a semi-infinite column. The approximate solution is also applied to an experimental breakthrough curve to estimate nonlinear denitrification parameters.

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## LABORATORY APPARATUS FOR STUDYING PESTICIDE LEACHING IN INTACT SOIL CORES

ISENSEE A R, SADEGHI A M

**Interpretive Summary:** Rainfall patterns (time between application and first rain event, intensity and duration), soil conditions, tillage practice and pesticide formulation are among the most important factors affecting pesticide leaching. Evaluation of these factors under field conditions is expensive, time consuming and subject to climatic variability. A laboratory method is needed to rapidly and accurately evaluate interactions between these factors as they impact pesticide leaching. This paper describes the design, construction, operation, and performance of an apparatus to study pesticide leaching through intact soil cores. A technique is described for mounting intact soil cores that nearly eliminates water movement at the soil-wall interface; a problem that often plagues soil column studies. A turntable is used to support and rotate up to 12 cores under a rain simulator capable of duplicating many rainfall rates. The capability for precise simulation of rainfall, accommodation of large numbers of soil cores and relatively fast set-up time make this apparatus ideal as a laboratory tool for conducting basic research.

**Technical Abstract:** This paper describes the design, construction, operation, and performance of an apparatus to study pesticide leaching through intact soil cores obtained from no-till (NT) and conventional-till (CT) corn fields. A technique is described for rapidly mounting intact soil cores. A turntable is used to support and rotate soil cores (up to 12) under an oscillating rain simulator capable of producing rainfall rates of 1 to 30mm/h. Each soil core is attached to a filtration flask which is connected to a -10 to -20 Kpa vacuum supply. The CV of the rainfall delivery rate over a range of 2-12 mm/h averaged 3.7%. Dye studies using intact soil cores indicated slower water movement at the soil-wall interface than through the soil matrix. An experiment conducted to evaluate atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] leaching through CT and NT soil cores indicated consistently greater leaching through CT cores and flawless operation of the apparatus. The capability of precise simulation of rainfall, accommodation of large number of soil cores, and ease of modification to meet a wide range of research parameters make this apparatus ideal for the laboratory evaluation of soil-water-pesticide interactions on pesticide leaching.

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## IMPACT OF TILLAGE PRACTICE ON SHALLOW GROUNDWATER QUALITY

ISENSEE ALLAN R, SADEGHI ALI M

**Interpretive Summary:** This paper describes the effect of no-till compared to conventional-till corn production practices on the leaching of atrazine, alachlor and cyanazine to shallow groundwater over a 5.5 year period in a field site at Beltsville, MD. Samples of unconfined (< 1.5 m deep) and confined (< 3 m and 4.5 to 11 m deep) groundwater were collected and analyzed for the pesticides at monthly intervals. Highest concentrations of all pesticides occurred in confined groundwater (< 3 m deep) soon after application under both tillage systems. Concentrations declined to low (atrazine) or nondetectable (alachlor and cyanazine) levels within three months. Rainfall timing and amount relative to pesticide application was critical to determining the magnitude of pesticide leaching to groundwater. The highest concentrations of the study were caused by a 4.8 cm rain that began 12 hours after application in 1988. This study indicates that more pesticide leaching to shallow groundwater occurs under no-till than conventional till, but peak levels exceeded health advisory levels only once in the study and residues decreased rapidly with time. Additionally, residues in deep wells (4.5 to 11 m) remained below the detection level indicating that these pesticides had not leached to this depth after as many as ten years of continuous pesticide application.

**Technical Abstract:** A field experiment was established in 1986 to assess the effect of conventional and no-till cultural practices on the movement of pesticides into shallow groundwater. Groundwater was sampled from unconfined (< 1.5 m deep) and confined (< 3 m and 4.5 to 11 m deep) monitoring wells in 1986-1991 and sampled for atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine], alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide], and cyanazine [2-[[4-chloro-6-(ethylamino)-1,3,5-triazine-2-yl]amino]-2-methylpropanenitrile]. Concentrations of pesticides were cyclical; residues were highest soon after application each year and then declined, alachlor and cyanazine to nondetectable levels within 3 mo. Atrazine residues, present in confined groundwater all year, ranged in concentrations between 0.03 to 1.9 and 0.16 to 3.4 ug/L for the NT and CT plots, respectively for 53 of 56 samplings over 5.5 y. Atrazine residues under fields treated before 1986 declined from < 0.5 ug/L in 1987-88 to < 0.01 ug/L by 1991. Pesticide residues were higher in unconfined than confined groundwater. Amount and timing of rainfall relative to pesticide application was critically important to pesticide leaching. The highest pesticide concentrations of the 5.5 y study were caused by a prolonged rain immediately after application in 1988 with concentration spikes ca. 4 to 50X greater under no-till than conventional till plots. Results of this study suggest that preferential transport occurred.

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## IMPACT OF TILLAGE PRACTICE ON RUNOFF AND PESTICIDE TRANSPORT

ISENSEE ALLEN R, SADEGHI ALI M

**Interpretive Summary:** Studies conducted to evaluate the effect of tillage practice on both the volume of runoff and pesticide loss in runoff have shown that no-till can either increase or decrease loss compared to conventional till. Most of those studies were conducted on small plots using rain simulators, often at high rainfall intensities. This study describes runoff and pesticide loss from relatively large no-till and conventional till plots from natural rainfall over two years. Runoff was measured, and samples were collected for atrazine, cyanazine and alachlor analyzes for 2 and 3 months after application in 1990 and 1991, respectively. Time between rainfall events was critical in controlling the amount of runoff. When rain events were more than 7 days apart, runoff was greater from no-till than conventional till. The reverse occurred when 7 or more days passed between rains. Pesticide concentrations in runoff and total loss were greatest for atrazine followed by cyanazine and alachlor. Concentrations of all pesticides were highest for the first runoff event after application and then decreased with each subsequent event. This study indicated that the soil moisture content at the time of a rain event may control the volume of runoff more than the tillage practice. The greater loss of pesticides from no-till may be due to surface crop residue in the no-till plots keeping the pesticides more available for runoff loss than bare soil in the conventional till plots.

**Technical Abstract:** A two-year study was conducted to evaluate the effect of no-till (NT) and conventional-till (CT) corn production practices on runoff and pesticide loss in runoff from natural rainfall. Runoff from duplicate NT and CT plots (0.25 to 0.5 ha) was measured and the water analyzed for atrazine, cyanazine and alachlor. Runoff of water was greater from NT than from CT plots when the time between rainfall events was less than 7 days, but runoff from CT was greater than NT when 7 or more days passed between rains. Atrazine and cyanazine concentrations were 2 to 10 times higher in runoff from NT than from CT; alachlor concentrations were unaffected by tillage. Concentrations of all pesticides were highest for the first runoff event after application and then decreased rapidly with each subsequent runoff. The time between application and the first runoff event was 3 and 8 days for 1990 and 1991, respectively, which resulted in 5 to 10 times higher concentrations of all pesticides in the first event for 1990 than 1991. Total loss (percent of applied) of atrazine, cyanazine and alachlor was 1.5, 1.6, and 0.3 (NT) and 1.0, 0.7, and 0.5 (CT), respectively, for 1990; corresponding losses for 1991 were 0.8, 0.6 and 0.2 (NT) and 0.3, 0.2 and 0.2 (CT).

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## THE GENES ENCODING S-TRIAZINE DEGRADATION ARE PLASMA ENCODED IN KLEBSIELLA PNEUMONIAE STRAIN 99

KARNS JEFFERY S, EATON RICHARD W

**Interpretive Summary:** Plasmids are extrachromosomal, self-replicating pieces of DNA that often encode genes which impart unique properties upon the bacteria in which they reside. Because they can be transferred between bacteria plasmids are a means by which genetic information can be rapidly shared by members of the soil microbial community. Thus, plasmids can be a part of the mechanism by which soil microbes evolve the ability to degrade agricultural chemicals. This study shows that the genes which encode the enzymes for the degradation of the simple s-triazine compounds ammelide and cyanuric acid are carried on a large plasmid in a strain of *Klebsiella pneumoniae*. This plasmid is capable of transfer to other bacteria, indicating that it may act as an agent in the evolution of s-triazine degradation capabilities in bacteria. Ammelide and cyanuric acid are likely intermediates in the degradation of the herbicides atrazine, cyanazine and simazine.

**Technical Abstract:** *Klebsiella pneumoniae* strain 99 degrades the s-triazine compound ammelide through cyanuric acid and biuret to yield urea, carbon dioxide and ammonia. The urea and ammonia formed from the degradation of ammelide or cyanuric acid are utilized as sources of nitrogen for growth of the organism. When plasmids of the IncI-alpha incompatibility group were transferred into *K. pneumoniae* strain 99 the ability to degrade s-triazine compounds was lost at high frequency.

Analysis of the plasmid profiles of s-triazine positive and s-triazine negative derivatives of strain 99 indicated that the largest of the at least 5 plasmids present in this organism carried the genes encoding the s-triazine degradation pathway. Conjugal transfer of this plasmid into a type strain of *Klebsiella planticola* resulted in exconjugants able to utilize ammelide or cyanuric acid as nitrogen sources. Thus, all the genes required for s-triazine degradation are present on a large IncI-alpha plasmid in *K. pneumoniae* strain 99.

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## BIOMINERALIZATION OF ATRAZINE OZONATION PRODUCTS. APPLICATION TO THE DEVELOPMENT OF A PESTICIDE WASTE DISPOSAL SYSTEM.

LEESON ANDREA, HAPEMAN CATHLEEN J, SHELTON DANIEL R

**Interpretive Summary:** Interpretive Summary: Concern for pesticide contaminated soils, wells, ground and surface waters has demanded development of remediation strategies. Research has demonstrated that oxidation transforms pesticides into materials that can be more easily mineralized (degraded to carbon dioxide, ammonia, inorganic salts, etc.) by microorganisms. The oxidized compounds are often used by the organisms as carbon sources and energy for growth, but this is not true for atrazine, the one of the most widely used herbicides in the U.S. Oxidation of atrazine using ozone gives rise to chlorodiamino-s-triazine (CAAT), which can be used only as a nitrogen source. Unfortunately, many pesticide waste mixtures also contain ammonia which is the preferred nitrogen source for most microorganisms. A bacterium (DRS-1) was isolated from sewage sludge that used CAAT as a nitrogen source, even in the presence of high ammonia concentrations. The rate of CAAT mineralization in the presence of different ammonia concentrations was determined. Kinetic constants for CAAT degradation by DRS-1, which are needed to optimize bioreactors in treatment systems, were estimated. Two bench scale bioreactors were fabricated and DRS-1 readily degraded CAAT under simulated field conditions. This study demonstrated that together, oxidation and microbial mineralization could readily convert atrazine to carbon dioxide and useful nitrogen compounds.

**Technical Abstract:** Development of remediation techniques for unusable pesticide wastes has led to a binary scheme involving ozonation followed by biomineralization of the resultant oxidized pesticides. Preliminary field tests of this technique indicated that the s-triazines were somewhat more recalcitrant than the other pesticides present. Further experiments identified the final ozonation products of atrazine, the most widely used s-triazine, as 4-acetamido-6-amino-2-chloro-s-triazine (CDAT) and chlorodiamino-s-triazine (CAAT). These compounds can be utilized by microorganisms only as nitrogen sources, however, 1% concentrations of ammonia fertilizers are not uncommon in pesticide waste. Therefore, the organism should prefer an organic nitrogen source and tolerate high ammonia concentrations. A gram positive rod, DRS-I, was observed to degrade CAAT in the presence of high ammonia concentrations (0.8 M) with the addition of a carbon source (corn syrup), in contrast to a known s-triazine degrading organism which could not. Near complete mineralization of CAAT to CO<sub>2</sub> by DRS-I was demonstrated using CAAT-U-ring-<sup>14</sup>C. Bench scale reactors indicated that continuous flow or fixed-film reactors would support growth of DRS-I cultures and CAAT degradation.

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## MOBILITY OF AGROCHEMICALS UNDER TWO TILLAGE SYSTEMS

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**Interpretive Summary:** During the last decade there has been a major shift by farmers from plow tillage (PT) towards conservation tillage and no-tillage (NT). Concern has been raised regarding the possibly greater leaching of chemicals to the ground water under conservation tillage. This laboratory study was conducted to determine the influence of recent PT versus long-term NT on the movement of bromide, nitrate, and four pesticides through surface soil under severe leaching conditions. Strong evidence was found for preferential flow through the soil, with the chemicals by-passing much of the soil-matrix under recently plowed soils and NT soils. Nitrate leaching was significantly greater under PT than NT, apparently due to the greater mineralizing activity of the PT. The higher organic matter content of the upper portion of the NT soil probably caused more adsorption of the pesticides. Caution should be exercised in generalizing from laboratory to field conditions, but his data suggests that there can be greater leaching losses of surface applied agrochemicals to groundwater under PT than under NT. This laboratory study provided additional insight on the influence of tillage on leaching of fertilizers and pesticides applied to agricultural soils, and should be most useful to scientists in planning further research.

**Technical Abstract:** The fate of agrochemicals is often greatly affected by the surface-soil conditions in the field. This study was conducted to characterize the impact of two contrasting tillage systems on the movement of agrochemicals in soil. The two tillage systems were plow-(PT) and no-tillage (NT) for corn (*Zea mays*, L.) production. The study included incubation and leaching of undisturbed soil columns and disturbed soil samples from 17-yr mono-tillage plots. The agrochemicals used in the study were  $\text{NH}_4\text{NO}_3$ , atrazine (2-chloro-4-ethylamino-6-isopropylamino- 1,3,5-triazine-2,4 diamine), carbofuran (2,3-dihydro-2,2- dimethyl-7-benzofuranyl methylcarbamate), diazinon (0,0-diethyl-0-(6-methyl-2(1-methylethyl)- 4-pyrimidinyl phosphor-othioate), and metolachlor (2-chloro-N-(2-ethyl -6-methylphenyl) -N-(2-methoxy-1-methylethyl) acetamide. The results of this study show greater ponded flow movement of all agrochemicals in soils under PT vs. NT conditions. Strong evidence was found for preferential flow through the soil, with the chemicals by-passing much of the soil-matrix under recently plowed soils as well as NT soils. Nitrate leaching was significantly greater under PT than NT, apparently due to greater mineralizing activity of the PT soil compared to the NT soil. The pesticide movement also tended to be greater under PT than NT. Caution should be exercised in generalizing to field conditions, but this data suggests that there can be greater leaching losses of surface applied agrochemicals to groundwater under PT than under NT.

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## IMPACT OF TILLAGE ON MICROBIAL ACTIVITY AND FATE OF PESTICIDES IN THE SOIL

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**Interpretive Summary:** The use of conservation tillage, and in particular no-tillage, has expanded greatly in the past decade. However, the impacts of conservation tillage on mobility of pesticides is still largely unknown. A laboratory incubation study was undertaken to evaluate the impacts of no-tillage vs. plow-tillage on pesticide degradation and subsequent mobility, using disturbed surface soil samples collected from long-term tillage plots from the Piedmont region of Maryland. The pesticides studied were isotope labelled atrazine, carbofuran, diazinon, and metolachlor. We found greater mobility of these pesticides in plow-tillage soil than in no-tillage soil. The lower mobility of pesticides in no-tillage was attributed to greater numbers of microbes and a greater activity of microbes which increased pesticide biodegradation. This is consistent with greater supply of residues and higher organic matter levels with no-tillage. This research is of interest to scientists and modelers who are interested in the transformation of pesticides as affected by modern tillage systems.

**Technical Abstract:** A study was made of the impact of two tillage systems, plow-tillage (PT) and no-tillage (NT), on microbial activity and the fate of pesticides in surface soil. The pesticides were atrazine, carbofuran, diazinon, and metolachlor. The study involved incubation of the pesticides in disturbed soil and the leaching of the pesticides from the soil after various periods of time. The soils were also treated with selective inhibitors of fungi or bacteria, with a total microbial-biocide, or were untreated to study the interaction between microbial communities in pesticide degradation. The biodegradation of ring C-14 labeled pesticides was also studied. Pesticide mobility was greater in PT soil than NT soil. Higher microbial populations and greater microbial activity in NT soil caused higher mineralization rates of atrazine, diazinon and carbofuran. Enhanced rates of biotransformation played an important role in reducing the mobility of metolachlor and carbofuran in NT soils. Synergistic effects between fungi and bacteria were observed in the degradation of atrazine and diazinon. Carbofuran, however, was also degraded in the soils where fungi were selectively inhibited. Possible mechanisms for enhanced biodegradation and decreased mobility of these pesticides in NT soil are discussed.

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## UGA IS NATURALLY SUPPRESSED IN WILD-TYPE BACILLUS SUBTILIS

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**Interpretive Summary:** The biochemical mechanisms that underlie the genetic processes of bacteria and more complex organisms are the focus of intense study worldwide. Within this realm of research are studies of the processes by which genetic information encoded on the DNA of an organism is deciphered so that such cellular material as proteins are made. Recombinant DNA techniques were used to demonstrate that the 'genetic punctuation' used to mark the location on DNA that protein synthesis should stop varies between two different important groups of bacteria. This study revealed that a DNA sequence, which functions as a genetic punctuation signal in many such organisms as the well studied intestinal bacteria *Escherichia coli*, is naturally ignored in the industrially important bacteria belonging to the group *Bacillus*. This finding is important to scientists who examine DNA while searching for important genes and to those who are trying to manipulate important genes so that they may be expressed in useful organisms.

**Technical Abstract:** The ochre codon UAA functions as a translation termination codon in *Bacillus subtilis*. Mutations in *B. subtilis* which suppress the ochre codon were found to insert lysine (sup-3 and sup-67) or leucine (sup-44). As with the ochre codon, the opal codon UGA, occurs at the end of several coding sequences that function in *B. subtilis* but not within coding sequences. This location is consistent with the assignment of UGA as a stop codon. However, if UGA were only a stop codon it should be expected that the extensive generation of random mutations in *B. subtilis* during the last three decades would have resulted in the insertion of UGA within a coding sequence. This class of mutation would have been revealed by the subsequent isolation of an extragenic suppressor, which predictably would fail to suppress UAA/UAG. Since all known nonsense suppressor mutations of *B. subtilis* suppress ochre and amber mutations these cannot suppress UGA. Thus either UGA has never been introduced into a coding sequence in *B. subtilis*, which is highly unlikely, or *B. subtilis* naturally suppresses UGA. By use of mutations within the cat-86 gene we show that UGA is naturally suppressed in each of four strains of *B. subtilis*. Weak suppression is also observed in *Staphylococcus aureus*. We demonstrate that in *B. subtilis* the suppression of UGA is due to insertion of tryptophan. The apparent efficiency of UGA suppression in *B. subtilis* ranges from about 1 to 6%.

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## EFFECT OF COVER CROPS ON GROUNDWATER QUALITY

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**Interpretive Summary:** Farmers face a difficult task as they seek to balance the competing goals of maintaining farm profitability, by ensuring an adequate supply of N to crops, yet avoiding excessive N rates that could increase nitrate losses to groundwater. Winter cover cropping is an important management practice that can reduce nitrate leaching into groundwater by: using water to reduce percolation, assimilating nitrogen to reduce soil nitrate, and through synchronized competition between the cover crop N uptake season vs the nitrate leaching season. A summary of the literature clearly shows that cover cropping can reduce nitrate leaching by 20 to 80% compared to no cover cropping. Furthermore, grass cover crops are two to three times more effective than legumes (hairy vetch, clovers, etc.) in reducing nitrate leaching. The value of cover cropping will be greatest in the Southeastern U.S. and in irrigated agriculture, but model simulation results predict that cover cropping will have a broadly beneficial impact over much of the U.S. Management practices which will improve nitrate conservation by cover cropping include selection of a species with vigorous fall growth and early planting. This review and analysis will be important to applied research scientists, extension agents, and soil conservationists as they plan and advise farmers on development of management systems to reduce nitrate losses into groundwater.

**Technical Abstract:** Winter cover crops can influence nitrate leaching and groundwater quality by: i) influencing the water budget ii) affecting the soil nitrate concentration, and iii) through synchronized competition during the water recharge season. Experimental results from the literature clearly show that cover crops can reduce both the mass of N leached, and the nitrate concentration of the leachate, by 20 to 80% compared to no cover crop. The grasses and brassicas are two to three times more efficient than legumes in reducing N leaching. Management factors which improve N conservation are selection of a species with vigorous fall growth and early cover crop establishment. Using the EPIC model it was estimated that a winter cover crop will have the greatest impact on nitrate leaching in the humid Southeast and in irrigated agriculture, but cover crops had a positive effect for all scenarios evaluated. Additional research needs include: more direct field measurements of nitrate leaching for a range of soils, cover crops, and climates; improved understanding and modeling of the N cycle; and improved plant germplasm for use as cover crops.

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## PREDICTING N FERTILIZER NEEDS FOR CORN IN HUMID REGIONS: UNDERLYING PRINCIPLES

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**Interpretive Summary:** Society is concerned about nitrate enrichment of groundwater. The agriculture community shares this concern and has made major improvements over the past 10 years in predicting fertilizer N needs for corn in humid regions. These improvements have involved: clarification of procedures to estimate expected yields, expanded use of the preplant soil nitrate test into humid areas, development and implementation of the pre-sidedress soil nitrate test, and the environmental evaluation and improvement of previous N recommendation systems. Adoption of the pre-sidedress soil nitrate test has been the most significant advance in humid region soil N testing in the past decade. This test is based on the timely monitoring of the field mineralization process and is well suited to warm-season crops and silt loam soils. This test can identify N sufficient sites i.e., sites needing little or no extra fertilizer N. The test will help extension agents, soil conservationists, and farmers identify N sufficient sites and thereby: conserve fertilizer N, improve N use efficiency, and reduce nitrate losses to groundwater.

**Technical Abstract:** Nitrogen is a mobile and dynamic nutrient, especially in humid climates. Predicting N fertilizer needs for corn in humid regions is based on N balance principles which result in N predictions being based on crop factors, soil N supply, and climatic factors. The crop factors are usually addressed through some type of predicted yield estimate, which offers the advantage of integrating many local production factors. However, this approach can also be greatly misused if careful attention is not given to definition of terms and the method used to actually estimate the expected yield. The soil N supply factors are usually assessed through a preplant soil NO<sub>3</sub>-N measurement, a general estimate of N mineralization through soil organic matter content, a N credit adjustment (e.g., legume or manure credit), or the use of the pre-sidedress soil nitrate test (PSNT). The NO<sub>3</sub>-N content of humid temperate soils growing corn exhibits rhythmic patterns of: low levels after winter leaching/denitrification, an accumulation of NO<sub>3</sub>-N in spring and early summer due to the resumption of mineralization, a dramatic decline in summer due to corn N uptake, and a modest increase in fall due to continued mineralization and no crop uptake. The underlying principles of the PSNT reveal that it is an in situ N mineralization test that is well suited for warm-season crops and fine-textured soils. Future improvements will likely include: i) expanded use of the PSNT, ii) inclusion of more site specific information, site weather or soil taxonomic data, and iii) expanded use of N management models to interpret soil N tests and integrate the complex factors affecting soil N transformations into a more fully unified system.

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PURIFICATION AND CHARACTERIZATION OF THE METHYLCARBAMATE HYDROLASE  
FROM  
PSEUDOMONAS STRAIN CRL-OK

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**Interpretive Summary:** Many studies have demonstrated that a variety of pesticides are degraded by enzymes produced by soil bacteria. One area of great interest in biotechnology is the use of these bacterial enzymes in degrading pesticide wastes. Some pesticides are effectively detoxified by a single enzymatic reaction, while others require a series of reactions before they are rendered nontoxic. A bacterial enzyme that hydrolyzes and detoxifies the methylcarbamate pesticide carbaryl was isolated and characterized in this study. While this enzyme was similar to a previously identified carbamate hydrolase, it differed from the known enzyme with respect to its size and substrate specificity. Further comparison of these enzymes may lead to a precise understanding of how they function and will aid efforts aimed at modifying such enzymes to increase their activities and substrate ranges.

**Technical Abstract:** *Pseudomonas* sp. strain CRL-OK was isolated from sewage sludge by enrichment using the insecticide carbaryl (1-naphthyl N-methylcarbamate) as a carbon source. A unique cytosolic enzyme that hydrolyzes the carbamate linkage of carbaryl was purified more than 1000-fold from cell-free extracts of strain CRL-OK. After purification, activity was stable for greater than one month at 4 C and stable indefinitely at -80 C. The hydrolase is composed of two identical subunits of 85,000 daltons and has temperature and pH optima of 60 C and 8.5, respectively. Its substrates include the N-methylcarbamate pesticides carbofuran and aldicarb, but not the phenylcarbamate CIPC, the thiocarbamate EPTC, nor the dimethylcarbamate o-NPDC. Hydrolase activity was not affected by the ionic detergent SDS at concentrations up to 0.2%, by 2-mercaptoethanol concentrations up to 0.2mM, nor by prolonged incubation in the presence of the divalent cation chelator EDTA.

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# THE ORGANOPHOSPHATE ACID ANHYDRASE GENE OPAB FROM THE GRAM-POSITIVE STRAIN B-1: CLONING, NUCLEOTIDE SEQUENCE, AND EXPRESSION IN E. COLI.

MULBRY WALTER W

**Interpretive Summary:** Parathion hydrolases are bacterial enzymes that carry out the first step of the degradation of many organophosphate pesticides. In this study a new parathion hydrolase gene was isolated and its DNA sequence was determined. Although the protein specified by this new gene has roughly similar substrate affinities to a previously characterized *Flavobacterium* parathion hydrolase, its enzymatic activity is much lower than the *Flavobacterium* enzyme. By carefully comparing the genes for these two enzymes scientists can begin to unravel the basis of their catalytic differences and may be able to design better enzymes for pesticide waste disposal.

**Technical Abstract:** The organophosphate acid (OPA) anhydases (previously termed parathion hydrolases) from the Gram-positive bacterial strain B-1 and *Flavobacterium* sp. ATCC 27551 display roughly similar affinities for the substrate ethyl parathion as well as similar pH and temperature optima. However the two enzymes are quite distinct with respect to their sizes, cellular locations, relative affinities for ethyl parathion and the structurally related organophosphate insecticide O-ethyl-O-4-nitrophenyl phenylphosphonothioate (EPN), and stimulation or inhibition by divalent cations and DTT. The first twenty amino-terminal residues of the purified strain B-1 OPA anhydrase were determined. Two degenerate oligonucleotide were synthesized and used in a DNA amplification reaction to generate a 73 base pair DNA fragment from the B-1 gene opaB. The nucleotide sequence of the 73 base pair fragment was determined and a nondegenerate oligonucleotide probe for the opaB gene was designed from this sequence. A 3.55 kilobase DNA fragment which hybridized to the opaB probe was cloned and the nucleotide sequence of a 1600 base pair region containing opaB was determined. Under control of the lac promoter of pUC19, opaB expression in *E. coli* cultures was approximately 15-fold higher than in strain B-1 under the opaB native promoter. Comparison of opaB and opd revealed no significant regions of homology at the nucleotide or amino acid sequence level.

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## INTERPOLATION OF SOIL HYDRAULIC PROPERTIES BY PIECEWISE POLYNOMIALS

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**Interpretive Summary:** Continuous and smooth relationships between hydraulic conductivity and matrix potential, and between moisture content and matrix potential are commonly constructed from a limited number of data points by some method of interpolation or approximation that unavoidably smooths the data. This may result in a significant loss of information. This in turn can have an impact on the results of water quality simulation models that use these smoothed data in calculations of water movement in soils. In this paper we present an improved method to interpolate water contents from soil matrix potentials that preserves the shape of the original data. In simulations of ponded infiltration, calculated results, using the improved method to represent the moisture release curves, were closer to measured data during early stages of infiltration than were results from simulations using another commonly used method of representing moisture release data.

**Technical Abstract:** Continuous and smooth relationships between hydraulic conductivity and matrix potential, and between moisture content and matrix potential are commonly constructed from a limited number of data points by some method of interpolation or approximation that unavoidably smooths the data. This may result in a significant loss of information. This in turn can have an impact on the results of water quality simulation models that use these smoothed data in calculations of water movement in soils. We present an improved method, utilizing a piece-wise polynomial, to interpolate water contents from soil matrix potentials at midpoints between pairs of measured data. This method preserves the shape of the moisture release curve. The results of simulations of ponded infiltration using the improved method to represent the moisture release curve are compared to results using a logistic equation to represent the moisture release curve. Predicted matrix potentials, using values from the piecewise polynomial, were closer to measured data during early stages of infiltration. The predicted infiltration rate, using values from the logistic function was much less than the measured infiltration rate or the rate predicted using the piecewise polynomial. This suggests that high infiltration rates usually attributed to macropores may be simulated using a more realistic description of the moisture release curve near saturation.

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## SPATIAL AND TEMPORAL VARIABILITY OF CARBOFURAN DEGRADATION IN SOIL

PARKIN TIMOTHY B, SHELTON DAN R

**Interpretive Summary:** Microbial degradation is an important fate of pesticides in soil. Thus, prediction of the fate of pesticides in the environment requires knowledge of the factors which control microbial degradation rates. This necessarily requires determination of the spatial and temporal variability associated with pesticide degradation rates in soil. Our study was designed to quantify the spatial and temporal variability associated with microbial degradation of the insecticide, carbofuran. We observed higher rates of carbofuran degradation were associated with samples collected in the row as compared to samples collected between corn rows. Soil water content and microbial biomass jointly influenced the kinetic patterns observed as well as the spatial variations of carbofuran degradation activity.

**Technical Abstract:** Loss of pesticide efficacy resulting from enhanced rates of microbial degradation has been observed with several pesticides including the insecticide carbofuran. Soils in which this phenomenon occurs are often referred to as "problem soils". There have been few studies of the spatial or temporal variability of carbofuran degradation. Our study was designed to evaluate the spatial variability of carbofuran degradation activity in a conventional-till and a no-till corn field, and to assess temporal variations of carbofuran degradation activity. Soil samples were collected at two positional locations in each field (in-row and between-row) at three times during the growing season. Within the planting furrow maximum rates of carbofuran degradation were higher and resulting half-lives of carbofuran (DT-50%) were lower than in samples collected between corn rows. Interactive effects of both microbial biomass and soil water content appeared to influence spatial variations in the degradation kinetics of carbofuran as well as the positional differences observed. Temporal variations in carbofuran degradation appeared to be dominated by soil water content. At this time it remains uncertain whether the observed increase in numbers of carbofuran degrading organisms, in the row, was in response to the banded application of carbofuran, or to increased carbon availability in the rhizosphere.

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## TEMPERATURE AND MOISTURE EFFECTS ON CARBOFURAN DEGRADATION IN SOIL

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**Interpretive Summary:** Prediction of the fate of pesticides in soil is of interest from an environmental (pollution) as well as an agricultural (efficacy, carryover) viewpoint. In addition to accounting for transport mechanisms, accurate prediction of the fate of pesticides in soil must also account for degradation due to microbial activity. Two environmental parameters which control microbial degradation of pesticides in soil are moisture and temperature. This study was designed to quantify the impact of soil moisture and temperature on the microbial degradation of the insecticide carbofuran. Soils were incubated at 7 soil water tensions over the range of 0.03 to 1.5 MPa, and at four different temperatures (10 degrees C to 30 degrees C). It was observed that degradation activity increased with increasing soil moisture. A mathematical relationship was derived which summarizes the response of carbofuran degradation activity. The response of carbofuran degradation to temperature was also well described by an exponential relationship, from which it was estimated that each 10 degrees C increase in temperature carbofuran degradation activity increased by a factor of 1.68. This study provides quantitative mathematical relationships required for development of predictive models of pesticide fate in soil.

**Technical Abstract:** This study was designed to quantify the impact of soil water content and temperature on microbial degradation rates of the insecticide carbofuran. Carbofuran degradation was determined by monitoring the  $^{14}\text{CO}_2$  production from carbonyl-labeled carbofuran amended soils. Soils were incubated at 7 soil water tensions over the range of 0.03 to 1.5 MPa, and at four different temperatures (10 degrees C to 30 degrees C). The sigmoidal degradation kinetics observed from these incubations were modeled using a general saturation model. From this analysis two summary parameters were computed; the maximum rate of carbofuran degradation and the time required for disappearance of 50% of the added carbofuran (DT-50%). For the moisture experiments both maximum rate of hydrolysis and DT-50% were accurately modeled by an exponential relationship ( $r^2$  of 0.9930 and 0.9720, respectively). The response of carbofuran degradation to temperature was also well described by an exponential relationship, from which it was estimated that the Q10 associated with the maximum rate was 1.68, and the Q10 for DT-50% was 1.89.

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## SPATIAL VARIABILITY OF MICROBIAL PROCESSES IN SOIL

PARKIN TIMOTHY B, SHELTON DANIEL R

**Interpretive Summary:** Microbial transformations of fertilizers and pesticides in the surface soil have a direct impact on the mass of the agrochemical which is susceptible to leaching losses. Thus, our greatest potential for controlling leaching losses of agrochemicals is through the management of these compounds in the surface soil. A variety of strategies have been employed to maximize the residence time of applied chemical in the surface soil, including: timing of application, formulation (e.g. slow release fertilizers and encapsulated pesticides), and the use of compounds which modify microbial activity in soil (e.g. nitrification inhibitors). While these strategies have met with some success, more precise quantification of the microbial transformations of agrochemicals is required to aid the development of improved management strategies. The high temporal and spatial variability exhibited by many microbial processes, in many cases, precludes precise quantification. This paper provides a general review of past work on the spatial variability associated with microbial processes in soil. This discussion focuses on the scale at which variability is expressed as well as the soil/environmental factors which impact variability. Basic strategies for dealing with variability are presented.

**Technical Abstract:** Prediction of the fate of agrochemicals in the environment requires knowledge of the factors which control microbial degradation rates. This necessarily requires determination of the spatial and temporal variability associated with pesticide degradation rates and fertilizer transformations in soil. This paper presents a summary of recent concepts in quantifying the spatial and temporal variability associated with microbial processes in soil, and reports on statistical procedures for the analysis and interpretation of data. The concepts developed in the general discussion of variability are illustrated by a presentation of a specific study of the factors contributing to the spatial and temporal variability associated with the microbial degradation of the insecticide carbofuran.

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## EXIT CONDITION FOR MISCIBLE DISPLACEMENT EXPERIMENTS

PARLANGE J, STARR J L, VAN GENUCHTEN M T, BARRY D A, PARKER J C

**Interpretive Summary:** Concern about soil and groundwater pollution has motivated the development and testing of mathematical models to predict how agricultural chemicals move through the unsaturated zone between the soil surface and the groundwater table. Computer models for field conditions are often tested in the laboratory under controlled conditions using relatively short (finite) soil columns. Results of such studies provide useful data for extrapolation to field-scale conditions, provided the particular features of a soil column are accounted for, notably the finite length of the column as opposed to the semi-infinite setting of a field soil profile. This paper presents several equations which may be used to minimize potential errors caused by the fact that laboratory soil columns have a finite length. Results are important for modelers and experimentalists using laboratory soil column experiments in efforts to mimic field-scale chemical transport processes.

**Technical Abstract:** The one-dimensional solute transport is analyzed with the convection-dispersion model, including first and zeroth order irreversible reaction. A simple analytical expression is derived for the residence concentration which depends explicitly on the exit conditions at the end of the soil column or layer. The validity of the flux concentration solution ignoring the finite length of the column is also discussed by relating the exit conditions to the Peclet number

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## EXIT CONDITION FOR MISCIBLE DISPLACEMENT EXPERIMENTS

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### Interpretive Summary:

Until now there has been uncertainty in one important aspect of modeling the movement of chemicals through soil columns. That uncertainty was the effect of the discontinuity that exists at the outflow end of column studies and its effect on the concentration of chemicals as they approached the end of the column. An analytical expression was derived for the total (resident soil) chemical concentrations across the length of the column that more accurately takes into account the flow conditions that are found at the outflow end of soil columns. The effects of different outflow conditions on the resident solute concentrations in a soil column were presented which demonstrate the magnitude of the effects under several common flow conditions. Finally, the analytical expression was generalized to cases that also undergo simultaneous irreversible zeroth or first order kinetic reactions.

**Technical Abstract:** The one-dimensional solute transport is analyzed with the convection-dispersion model, including first and zero order irreversible reaction. A simple analytical expression is derived for the residence concentration which depends explicitly on the exit conditions at the end of the soil column or layer. The validity of the flux concentration solution ignoring the finite length of the column is also discussed by relating the exit conditions to the Peclet number.

Submitted to:(approved 09/04/91) SOIL SCIENCE

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## USING THE SIERPINSKI CARPET ALGORITHM TO CALCULATE SATURATED CONDUCTIVITY

RAWLS WALTER J, BRAKENSIEK DONALD L

**Interpretive Summary:** The saturated hydraulic conductivity is the most critical soil property for describing infiltration. A new saturated conductivity formulation using fractal processes was calibrated and validated for over 1100 soils. The procedure produces conductivity estimates which are within one standard deviation.

**Technical Abstract:** An equation for predicting saturated hydraulic conductivity was developed by coupling the Sierpinski carpet algorithm with the Marshall saturated hydraulic conductivity formulation. The parameters available porosity ( $e$ ) pore class interaction exponent ( $x$ ) and the number of pore classes ( $n$ ) were derived to represent a wide range of soils. The formulation was tested against over 1100 measurements and predicted saturated hydraulic conductivities within one standard deviation.

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## TEMPORAL VARIABILITY OF INFILTRATION FOR AGRICULTURAL SYSTEMS

RAWLS WALTER J, ONSTAD CHARLES A, BRAKENSIEK DONALD L

**Interpretive Summary:** Rainfall simulation experiments were conducted on a Barnes loam and Bearden silty clay loam at planting, midseason and harvest to determine the effect of rainfall intensity, prior crops, bare ground, crop canopy, residue and a combination of crop canopy and residue on the temporal steady state infiltration rate. The results illustrate that agricultural systems cause significant temporal effects on infiltration which needs to be incorporated into infiltration models in order to evaluate the effect of agricultural systems on runoff, erosion and water quality.

**Technical Abstract:** Rainfall simulation experiments were conducted on a Barnes loam and Bearden silty clay loam at planting, midseason and harvest to determine the effect of rainfall intensity, prior crops, bare ground, crop canopy, residue and a combination of crop canopy and residue on the temporal steady state infiltration rate. The steady state infiltration rate of bare ground decreased and then stabilized over the season. Canopy and residue maintained a higher steady state infiltration rate than that of bare ground, however, they did not produce an accumulative effect. Increases in rainfall intensity increased the steady state infiltration rate of bare ground. Plowing under sod increased the steady state infiltration rate; however, this effect was not maintained over the season.

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## A MODIFIED MARSHALL EQUATION FOR PREDICTING MATRIX AND MACROPORE SATURATED HYDRAULIC CONDUCTIVITY

RAWLS WALTER J, BRAKENSIEK DONALD L, LOGSDON SALLY D

**Interpretive Summary:** The prediction of the movement of water through the soil is needed to quantify the effects of agricultural practices on water quality. A prediction model based on pore size distribution was developed that predicted the hydraulic conductivity of the soil and macropores independently. This model allows us to evaluate specifically the effect of agricultural practices on the pore distribution and thus developed agricultural systems accordingly.

**Technical Abstract:** Equations for predicting matrix and macropore saturated hydraulic conductivity were developed by coupling the Sierpinski carpet algorithm with the Marshall saturated hydraulic conductivity formulation. The parameters matrix and macropore porosity, maximum pore radius, and the number of pore classes are related to soil properties to enable the equations to be used for a wide range of soils.

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## ACCLIMATION OF YOUNG SOYBEAN PLANTS TO HIGH CO<sub>2</sub> LEVEL INCREASES THE FOLIAR CO<sub>2</sub> COMPENSATION POINT AND DARK RESPIRATION RATE

ROBINSON J MICHAEL

**Interpretive Summary:** As part of a continuing effort to understand the influence of elevated atmospheric CO<sub>2</sub> levels on future crop plant productivity, a BARC scientist has studied how elevated CO<sub>2</sub> levels will influence the photosynthetic and respiratory metabolism in soybean plant leaves. When soybean plants were acclimated to concentrations of CO<sub>2</sub> above 350 parts per million (ppm), for example 1000 ppm, there was an increase in their foliar photosynthetic CO<sub>2</sub> assimilation rate as much as 1.5 times, which ultimately resulted in a doubled biomass accumulation. In high CO<sub>2</sub> plants, there was a dramatic increase in the CO<sub>2</sub> concentration point where leaf CO<sub>2</sub> assimilation and respiration rates are just balanced, and that this was a reflection of elevated foliar mitochondrial respiration in the light. In high CO<sub>2</sub> exposed plants, the higher foliar respiration rate apparently was brought on by increased levels and availability of respiratory substrates, e.g. sucrose and starch. Increased plant growth was positively correlated with the increased foliar respiration rate. It was found that there was no inhibition of maximal foliar CO<sub>2</sub> assimilation capacity in leaves of high CO<sub>2</sub> soybean plants. Comparative measurements of foliar net CO<sub>2</sub> photoassimilation rate as a function of CO<sub>2</sub> concentration revealed that there was a repression of the ability of the source leaves of high CO<sub>2</sub> soybean plants to absorb, transport and/or concentrate CO<sub>2</sub> when CO<sub>2</sub> was present at levels below 600 ppm. However, this did not inhibit plant growth in high CO<sub>2</sub> plants, since their foliar CO<sub>2</sub> absorption mechanism(s) had adapted to the presence of 1000 ppm CO<sub>2</sub>. This research provides data to plant ecologists and crop modelers to enable them to predict plant behavior at elevated CO<sub>2</sub> levels.

**Technical Abstract:** A study was undertaken to further examine the influence that high CO<sub>2</sub> acclimation exerts on soybean foliar photosynthetic carboxylation capacity, CO<sub>2</sub> compensation concentration (in the light), and dark respiration. Glycine max (L.) Merr. cv Amsoy plants were propagated in growth chambers maintained with 650  $\mu\text{E}/\text{m}^2\cdot\text{s}$  white light, 14 h light-10 h dark cycle, 27°C continuous, and 65% RH, for 10 days post-emergence (PE) in an ambient atmosphere containing 350 ppm CO<sub>2</sub> (normal CO<sub>2</sub> plants). At 10 days PE one-half of the plants were transferred to a growth chamber with identical conditions except that the atmosphere in the chamber contained CO<sub>2</sub> at 1000 ppm; these plants were acclimated for 12 additional days (high CO<sub>2</sub> plants). CO<sub>2</sub> enrichment of soybean plants increased CO<sub>2</sub> photoassimilation rate and doubled biomass accumulation. There was a dramatic increase in the foliar CO<sub>2</sub> compensation concentration (measured in the light), and this was a reflection of elevated foliar mitochondrial respiration in the light. In high CO<sub>2</sub> exposed plants, the higher foliar respiration rate apparently was brought on by increased levels and availability of respiratory substrates, e.g. foliar sucrose. Comparative measurements of foliar net CO<sub>2</sub> photoassimilation rate as a function of CO<sub>2</sub> concentration revealed there was a repression of the ability of the source leaves of high CO<sub>2</sub> soybean plants to absorb, transport and/or concentrate CO<sub>2</sub> when CO<sub>2</sub> was present at levels below 600 ppm. However, this didn't inhibit plant growth in high CO<sub>2</sub> plants, since their foliar CO<sub>2</sub> absorption mechanism(s) adapted to the presence of 1000 ppm CO<sub>2</sub>.

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## ACCLIMATION OF SPINACH PLANT FOLIAR PHOTOSYNTHETIC CARBON METABOLISM AND DARK RESPIRATION TO ELEVATED ATMOSPHERIC CO<sub>2</sub> LEVEL

ROBINSON J MICHAEL

**Interpretive Summary:** As part of the continuing effort to understand the influence that elevated atmospheric CO<sub>2</sub> levels will exert upon future crop plant productivity, an ARS scientist has undertaken the study of how elevated CO<sub>2</sub> levels will influence the photosynthetic and respiratory metabolism in spinach plant leaves. When spinach plants were acclimated to high CO<sub>2</sub> concentrations, e.g. 1000 parts per million (ppm), and compared with control plants simultaneously grown at normal CO<sub>2</sub> levels, e.g. 350 (ppm), there was as much as a 1.4-fold increase in their rates of photosynthetic CO<sub>2</sub> assimilation in leaves. Higher photosynthesis rates in the leaves of high relative to normal CO<sub>2</sub> plants ultimately resulted in a doubled dry mass per plant. As in the case of high CO<sub>2</sub> acclimated soybean, there was a dramatic increase in the CO<sub>2</sub> concentration point (where leaf CO<sub>2</sub> assimilation and respiration rates are just balanced) and this was a reflection of elevated foliar mitochondrial respiration in the light. The higher foliar respiration rate apparently was brought on by increased levels and availability of respiratory substrates, e.g. sucrose and starch. Activities of leaf photosynthetic enzymes, e.g. ribulose-1,5-bisP carboxylase (Rubisco), were 1.2-1.5 times higher in chloroplasts prepared from high compared with normal CO<sub>2</sub> plant leaves. Thus, in high CO<sub>2</sub> adapted plants, increased CO<sub>2</sub> fixation was due mainly to the higher CO<sub>2</sub> level available to Rubisco, but increased activities of plastid enzymes may have been a contributing factor. This research provides information to plant ecologists and crop modelers to enable them to predict plant behavior at elevated CO<sub>2</sub> levels.

**Technical Abstract:** Foliar photosynthetic metabolism and respiration rates were examined in *Spinacia oleracea* cv Wisconsin Dark Green plants which were exposed to high CO<sub>2</sub> levels for 15 days beginning at 21 days after emergence of the plants. At 21 days post-emergence, plants were acclimated for 15 additional days in high CO<sub>2</sub> (1000  $\mu$ l CO<sub>2</sub>/l air) with control plants at normal CO<sub>2</sub> (350  $\mu$ l CO<sub>2</sub>/l air). Typical source leaf net photosynthesis rates (expressed as  $\mu$ mol CO<sub>2</sub> fixed per dm<sup>2</sup>.h) in high and normal CO<sub>2</sub> plants were, respectively, 1034  $\pm$  40 (measured in 1000  $\mu$ l CO<sub>2</sub>/l air) and 751  $\pm$  54 (in 350  $\mu$ l CO<sub>2</sub>/l air). In high relative to normal CO<sub>2</sub> plants, growth rate was doubled, and leaf photosynthate levels, e.g. sucrose, were 1/3 higher. High carbohydrate status caused mitochondrial (dark) respiration rates, apparently ongoing in light, to double in magnitude. Activities of ribulose-1,5-bisP carboxylase (Rubisco), fructose-1,6- bisphosphate (C-1) phosphatase, and glyceraldehyde-3-phosphate dehydro- genase were 1.2-1.5 times higher in chloroplasts prepared from high compared with normal CO<sub>2</sub> plant leaves. There was no additional activity of Rubisco conferred by supplying excess units of carbonic anhydrase. Thus, in high CO<sub>2</sub> adapted plants, increased CO<sub>2</sub> fixation was due mainly to the higher CO<sub>2</sub> level available to Rubisco, but increased activities of plastid enzymes may have been a contributing factor. Higher foliar "dark", or mitochondrial respiration rate, ongoing in the light, suggested an increased photosynthate (anaplerotic) flow into the tricarboxylic acid cycle.

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## EFFECT OF TILLAGE SYSTEMS AND RAINFALL PATTERNS ON ATRAZINE DISTRIBUTION IN SOIL

SADEGHI A M, ISENSEE A R

**Interpretive Summary:** Atrazine is a widely used herbicide for the control of weeds in corn production. Variable levels of atrazine residues in soil of the rooting zone of corn and shallow groundwater have been reported under various agricultural tillage systems. The two-year (1987 & 1988) field data were analyzed to evaluate the effects of conventional and no-till practices, and their interactions under different climatic regimes on the distribution and leaching characteristics of atrazine in corn production. Overall, atrazine residues within the top 10 cm soil depth of conventional-till plots were higher than in the no-till plots, regardless of the difference in the rainfall patterns. The approximately two fold higher mean atrazine residues in the conventional-till plots over no-till plots in 1988 were most likely related to the rainfall that began 12 h after application. In contrast, in 1987, it did not rain until 3 to 4 days after application and the differences were not so great.

**Technical Abstract:** High variability of atrazine residues in soil and shallow groundwater have been reported under various agricultural management systems. This two-year study was conducted to evaluate atrazine residue levels in soil as influenced by no-till (NT) vs conventional-till (CT) under natural rainfall conditions. Atrazine was applied annually at the rate of 1.34 kg/ha to two NT and two CT plots one day after planting corn. Atrazine residues within the 0-10 cm soil depth of CT plots were higher than in the NT plots, regardless of the difference in the rainfall patterns. Higher (ca. 61%) mean atrazine residues in the CT plots than NT plots in 1988 was most likely related to the rainfall that began 12 h after application. In contrast, in 1987, it did not rain until 3 to 4 days after application and the residues in the CT were only 31% higher than in NT. These results indicate that even a subtle difference in the temporal rainfall distribution can result in a marked effect on the spatial distribution of atrazine.

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## **SPATIAL DISTRIBUTION OF ATRAZINE RESIDUES IN SOIL AND SHALLOW GROUNDWATER: EFFECT OF TILLAGE AND RAINFALL TIMING.**

**SADEGHI ALI M, ISENSEE ALLAN R**

**Interpretive Summary:** The combined effect of tillage and rainfall timing on the movement and distribution of pesticides has not been clearly understood. Residue values in the 0 - 30 cm soil depth and in shallow groundwater in 1987, 1988, and 1989 were used to demonstrate this interactional effect on the spatial distribution of atrazine in corn production. These three years were selected since nearly the same amount of rain fell, but at different times and intensities, within the period between atrazine application and the first sampling. Overall, the average atrazine residues in the top 10 cm soil of conventional-till plots were much higher than in no-till plots in all years, regardless of the rainfall timing. Highest atrazine residue levels in shallow groundwater were found in the samples collected from the no-till plots three days after the first rain event in 1988. However, the concentrations decreased markedly by 14 and 40 days post-application. The relatively high residue levels in 1988 presumably resulted from the first rain event in which contributed 48 mm of precipitation fell in a two-day rain that began twelve hours after application and lasted about 2 days. The average residue levels of atrazine in the wells below the clay layer in the no-till plots were higher than in the conventional-till plots in all three years.

**Technical Abstract:** A study was initiated in 1986 to compare the effects of no-till (NT) and conventional-till (CT) corn production on the movement of pesticides to groundwater. Specifically, the effect of rainfall timing on the spatial distribution of atrazine in the 0 - 30 cm soil depth and in groundwater less than 1 m deep was evaluated in 1987, 1988, and 1989. Nearly the same amount of rain fell, but at different times and intensities, between application and first sampling during these years. The average atrazine residues in the top 10 cm soil of the CT plots were much higher than the NT plots in all years. The difference was 23% in 1987 (first rain was 3 d after application), 56% in 1988 (12 h after application), and 63% in 1989 (6 d after application). Atrazine levels were 663 and 424 ug/L in samples collected from wells above the clay layer in the NT plots three days after the first rain in 1988. Concentrations decreased to 133 and 105 ug/L and 6 and 5 ug/L after 14 and 40 days. The high residues in 1988 resulted from 48 mm precipitation that fell over 2 days beginning 12 h post-application. The average levels of atrazine in the wells below the clay layer in the NT plots were higher than the CT plots in all years. The semivariograms for residues in the 0 to 30 cm soil depth showed that the residue values were spatially related for the separation distance of less than 16 m. For the well water samples, this distance was estimated to be about 30 m.

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## ROOT EXTRACTION OF NUTRIENTS ASSOCIATED WITH LONG-TERM SOIL MANAGEMENT

SHARPLEY A N, MEISINGER J J, POWER J F, SUAREZ D L

**Interpretive Summary:** One of the main challenges facing agricultural research at the present time, is to identify farming practices that will maintain long-term soil fertility and crop yields, while at the same time allowing a reduction in the amount of fertilizer chemicals added and number of tillage operations. From our current knowledge of processes determining the uptake of nutrients by crops, several areas of research are needed to meet this challenge. These areas of research involve determining the effect of tillage practice, fertilizer type and placement, residue management, and crop selection on the amount of water and plant available nutrients in the volume of soil where roots are actively growing. Results from this research should enhance the sustainability of agricultural production systems.

**Technical Abstract:** One of the main challenges of agricultural research is to identify management practices that maintain long-term soil fertility and crop production with reduced chemical inputs and tillage operations. This paper reviews the current state of knowledge and research needs concerning the impact of soil management on the root extraction of nutrients. Manageable variables controlling soil-water content, nutrient availability, root growth and development, and thereby, root extraction of nutrients are interactive, complex, and dynamic. There is, thus, a need for team research involving physical, chemical, and biological disciplines. This should focus on tillage practice, fertilizer type and placement, residue management, and crop selection to coincide the positional availability of soil water and nutrients during periods of active root growth and nutrient uptake. It is also important to determine the relative importance of soil properties on organic matter cycling as influenced by soil fauna and flora, tillage, and crop rotation. Information from identified research needs and integration of existing knowledge into management systems should facilitate progress towards enhancing sustainable soil fertility.

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## ROOT EXTRACTION OF NUTRIENTS ASSOCIATED WITH LONG-TERM SOIL MANAGEMENT

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**Technical Abstract:** One of the main challenges of agricultural research is to identify management practices that maintain long-term soil fertility and crop production with reduced chemical inputs and tillage operations. This paper reviews the current state of knowledge and research needs concerning the impact of soil management on the root extraction of nutrients. Manageable variables controlling soil-water content, nutrient availability, root growth and development, and thereby, root extraction of nutrients are interactive, complex, and dynamic. There is, thus, a need for team research involving physical, chemical and biological disciplines. This should focus on tillage practice, fertilizer type and placement, residue management, and crop selection to coincide the positional availability of soil water and nutrients during periods of active root growth and nutrient uptake. It is also important to determine the relative importance of soil properties on organic matter cycling as influenced by soil fauna and flora, tillage, and crop rotation. Information from identified research needs and integration of existing knowledge into management systems should facilitate progress towards enhancing sustainable soil fertility.

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## INFLUENCE OF RAINFALL INTENSITY AND CROP RESIDUE ON LEACHING OF ATRAZINE IN INTACT NO-TILL SOIL CORES

SIGUA GILBERT C, ISENSEE ALLAN R, SADEGHI ALI M

**Interpretive Summary:** Pesticides applied to no-till (NT) fields are often intercepted by a combination of crop residue and living vegetation. The effect this residue has on pesticide leaching as a function of rainfall amount and intensity is not well known and is the objective of this research. Intact soil cores (with crop residue) from NT fields were treated with <sup>14</sup>C atrazine and subjected to two pore volumes of simulated rain applied at 3 to 12 mm/h. The crop residue on a second set of intact soil cores was adjusted from 0 to 8000 kg/ha, treated with <sup>14</sup>C atrazine and subjected to two pore volumes of rain at 9 mm/h. Atrazine leaching through a third set of soil cores covered with dead compared to freshly harvested crop residue was evaluated as above. Both the amount and rate of atrazine leaching were greater at high (9 and 12 mm/h) compared to low (3 and 6 mm/h) rainfall intensities. Increasing amounts of crop residue from 2000 to 8000 kg/ha (25 to 100% of normal crop residue levels) decreased leaching of atrazine through soil cores. Freshly harvested crop residue reduced leaching more than dead crop residue. These results help explain observed variability in field experiments and indicate that potential pesticide leaching under field conditions is highly dependent on interactions between field conditions and rainfall amount and intensity.

**Technical Abstract:** We investigated the effect of rainfall intensity and crop residue on <sup>14</sup>C-labeled atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and bromide movement through no-till (NT) soil cores. Undisturbed soil cores (10 cm diameter by 8 cm deep) were taken from the surface of a NT corn field, surface treated with 1.3 kg/ha atrazine and 150 kg/ha KBr and subjected to uniform amounts of simulated rainfall at 3, 6, 9, or 12 mm/h. The crop residue on another set of cores was adjusted from 0 to 8000 kg/ha, treated with atrazine as above and subjected to 9 mm/h simulated rain. A third experiment compared recently harvested vegetation to dead crop residue on their effect on atrazine leaching. Overall, the transport of surface applied atrazine and Br were significantly ( $p < 0.01$ ) affected by rainfall intensity and crop residue. An average of 56% and 3.8% and 36% and 2.3% of the applied atrazine and Br were leached at the 12 mm/h and 3 mm/h rates, respectively. Covering soil cores with 2000 to 8000 kg/ha of crop residue reduced atrazine leaching by 19 to 28%, respectively, compared with cores without crop residue. Soil cores covered with 8000 kg/ha recently harvested vegetation reduced atrazine leaching 57% compared to cores covered with comparable amounts of dead crop residue.

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## ESTIMATION OF RATES OF GRANULAR CARBOFURAN DISSOLUTION IN SOIL

SHELTON DANIEL R, SADEGHI ALI M, ISENSEE ALLEN R

**Interpretive Summary:** Soil-borne insect pests are a major threat to crop (corn) production. Unlike foliar insect pests, which are amenable to integrated pest management techniques, soil applied granular pesticides are required for control of soil-borne insects. The use of biodegradable pesticides is desirable in order to minimize the potential for groundwater contamination. However, soil-applied pesticides which are degraded rapidly can result in a loss of efficacy and hence, significant yield losses. The development of pesticides of moderate persistence, or the implementation of management strategies using non-persistent pesticides, is dependant on accurate information regarding rates of biodegradation, minimum lethal pesticide concentrations, and rates of release of pesticides from granules. Previous studies have documented rates of microbial degradation and lethal pesticide concentrations. However, no studies have documented rates of pesticide leaching/dissolution from granules. This study provides quantitative data on the rate of release of pesticides from granules. This information may be used to develop methods for minimizing pesticide contamination while also maximizing pesticide efficacy.

**Technical Abstract:** Losses of efficacy of carbofuran are due to rates of microbial degradation which exceed rates of granular leaching/dissolution, resulting in carbofuran concentrations below the lethal threshold needed for control. Rates of carbofuran leaching from granules as a function of rainfall intensity/infiltration rate, and granular dissolution as a function of time, were estimated using a rain simulation device. Rates of leaching (1.5 ug/mg granules normalized to 1 cm/hr) were positively correlated with rainfall/infiltration. Rates of granular dissolution were linear up to 72 hrs (0.28 ug/mg granule. Adjusted for field conditions, ca. 50 hrs of rainfall would be required to leach carbofuran from granules or ca. 11 days (at field capacity) for dissolution of granules. Soil solution concentrations would be ca. 16 ppm, or 4 ppm bulk soil. Rates of spherical carbofuran diffusion from a theoretical granule were calculated. Carbofuran concentrations decreased rapidly as a function of distance. However, these high localized carbofuran concentrations may result in high population densities of carbofuran-degrading microorganisms in the vicinity of granules. These data suggest that losses of efficacy may result either from the complete leaching/dissolution of granules and biodegradation before larvae hatch, or rates of biodegradation which exceed rates of granular leaching/dissolution after larvae hatch.

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## ENZYME-BASED STRATEGY FOR TOXIC WASTE TREATMENT AND WASTE MINIMIZATION

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**Interpretive Summary:** Biotechnology promises to provide new and innovative processes for the disposal of waste agrochemicals. In some cases, the use of enzymes in waste treatment processes may have advantages over the use of whole organisms. Enzymes derived from recombinant organisms should have fewer regulatory hurdles to clear before they can be used. This is, in part, due to the fact that enzymes do not replicate and hence have finite lifetimes once applied. Before an enzyme can be used in any process the factors affecting the rate and extent of its degradation of the target compound must be determined. This study used the degradation of the insecticide coumaphos in waste cattle dips by parathion hydrolase as a system for the modeling of an enzyme-based waste treatment scenario. Parathion hydrolase was shown to be able to selectively remove a toxic metabolite of coumaphos, potasan, when enzyme concentrations were limited. This was shown to be due to potasan's increased solubility in water. Mathematical models considering enzyme half-life, temperature, and coumaphos and potasan concentrations, were derived which allow end users to determine how much enzyme needs to be added to any volume of cattle-dip to accomplish either the elimination of potasan from material still being used or the elimination of both potasan and coumaphos from waste material.

**Technical Abstract:** The increasing amounts of pesticides used throughout the world as well as the increasingly stringent governmental regulations concerning waste disposal mandates improved techniques of waste disposal and minimization. In this paper, parathion hydrolase, an enzyme with proven effectiveness at hydrolyzing organophosphate, was used to treat a cattle-dipping liquid containing the pesticide coumaphos, which is used to kill a disease-causing tick. Waste is generated from this process when a toxic dechlorination product of coumaphos, potasan, accumulates to concentrations hazardous to the cattle. This pesticide system was used as a model to demonstrate how enzyme technology can be applied to waste treatment and minimization. Kinetic experiments showed that the hydrolysis of the two organophosphate substrates can be modeled as first order reactions with identical rate constants. It was further shown that the enzyme is capable of hydrolyzing only dissolved substrates. Because of the eight-fold greater solubility of potasan than coumaphos (16.9 vs 2.2  $\mu\text{mol/L}$ ) it was possible to utilize the enzyme to selectively hydrolyze potasan. Thus, by limiting the amount of enzyme it is possible to selectively remove potasan to extend the lifetime of the cattle-dipping liquid, thereby reducing the amount of waste generated. Based upon experimental results, a mathematical model describing the system was developed and verified. The mathematical model was then used to simulate the ability of the enzyme to hydrolyze the total amount of organophosphate, and to selectively degrade all of the toxic potasan without a significant loss of coumaphos.

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## INFLUENCE OF SAMPLE VOLUME ON NITRATE-N MEASUREMENTS

STARR JAMES L, PARKIN TIMOTHY B, MEISINGER JOHN J

**Interpretive Summary:** The volume of soil sampled for chemical analysis may be important for agrochemicals that undergo rapid transformations, especially if the soil concentrations are highly dependent on environmental conditions that can change abruptly within a small spatial area. The purpose of this study was to investigate the influence of six sample volumes on the magnitude and variability of several commonly measured surface soil parameters. This paper presents the results for the agrochemical and plant nutrient, nitrate-nitrogen. The smallest sample volume (slightly smaller than the most commonly used hand sampler) was often too small to accurately estimate the statistical parameters for soil nitrate-N. The smallest sample volume also required 20 to 50 percent more samples than the larger samplers to achieve satisfactory estimates of the sample mean. No clear trends in parameter estimation occurred across the range of larger sample volumes. This research provides better guidelines for the size of soil samplers that should be used to most clearly characterize the nitrate-N levels in a surface soil.

**Technical Abstract:** The influence of sample volume on the magnitude and variability of soil NO<sub>3</sub>-N levels was investigated at Beltsville, MD, on a Beltsville silt loam soil (Typic Fragiudult). Five soil cores, ranging in volume from 38 to 366 cm<sup>3</sup>, and block samples of 8770 cm<sup>3</sup> were collected from plow- and no-till plots before and after planting corn (*Zea mays* L.). Nearly all the NO<sub>3</sub>-N values were lognormally distributed. The magnitude of skewness was related more to NO<sub>3</sub>-N concentration than to sample size, except for the largest size (8770 cm<sup>3</sup>) which was always minimally skewed. The smallest sample volume was often too small to accurately estimate the statistical parameters for soil nitrate-N, and required 20 to 50 percent more samples than the larger sample volumes to achieve satisfactory estimates of the sample mean. No clear trends in parameter estimation occurred across the range of larger sample volumes.

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## THE CALCULATION OF OPTIMUM NITROGEN FERTILIZATION RATES IN THE DEVELOPMENT OF NUTRIENT MANAGEMENT PROGRAMS

TAYLOR A W, WEISMILLER R A, WOODWARD M D, MEISINGER JOHN J

**Interpretive Summary:** Throughout the Chesapeake Bay region nutrient management planning has formed the basis for more accurate forecasts of corn fertilizer N needs. The goal of these plans is to maintain a profitable agriculture while lowering environmental impacts. However, it must be realized that agriculture's environmental impact will never be entirely eliminated due to the complexities of the agriculture N cycle and uncertainties in rainfall. The N management plans are based on a careful N accounting of major N credits and debits. The N debit calculation is based on the realistic yield goal of the field. Nitrogen credits are then calculated for manure additions, based on manure analysis, and for previous legume crops. The final N accounting forecasts the need for supplemental fertilizer N. The final decision for fertilizer N can be checked with the pre-sidedress soil nitrate test which measures the nitrate concentration in the surface foot of soil when the corn is about 12 inches tall. This N soil test has successfully identified sites that are N sufficient and therefore can save over-application of fertilizer N. Future work will require further field testing and evaluation of these nutrient management systems.

**Technical Abstract:** Improved methodology for the calculation of the optimal amounts of corn fertilizer N has formed the basis for Nutrient Management Planning throughout the Chesapeake Basin. The objective of these plans is to maintain a viable agriculture while lowering environmental impacts, although it must be recognized that owing to uncertainties in weather these impacts can never be entirely eliminated. The general form of the N management plan involves estimating the crop N requirement, the N credit for manure, and the N credit for crop rotations. The corn N requirement is estimated from the expected yield (in bu/a) multiplied by a factor of 1.0 lbs N/bu. Manure N credits are calculated from a manure analysis and actual application rates based on a calibrated manure spreader. Legume N credits are evaluated from the type of legume and the vigor of the stand. The adequacy of the forecasted N rate can be checked with the pre-sidedress N soil test which measures the nitrate-N content of the surface foot of soil when the corn is 12 inches tall. Future research in this area must include improvement and calibration of these predictive techniques and newer soil N tests. This continued research will require a commitment to applied field research.

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## SOLUTE LEACHING IN CROP ROW VS. INTERROW ZONES

TIMLIN DENNIS J, HEATHMAN GARY C, AHUJA LJ

**Interpretive Summary:** This was a pilot study to investigate differences in overall solute leaching from soil beneath row vs interrow zones of a row crop and help identify management practices to reduce solute leaching. Two crops were used, corn and soybean. A water soluble tracer was applied uniformly to the soil surface. In the fine sandy loam half of the corn plot there was significantly more leaching of the tracer in the interrow positions than in the row positions. The differences were not significant in the clayey areas of both plots and in the sandy area planted to soybean. Overall leaching was significantly less under soybean than under corn. Further research that will take advantage of these results should be carried out to develop management strategies to minimize leaching of chemicals from the soil below row crops.

**Technical Abstract:** This was a pilot study to investigate overall differences in solute leaching from soil beneath row vs. interrow zones of a row crop, which could be utilized to minimize overall leaching. Strontium bromide was uniformly applied to 7 by 6 m plots planted to corn and soybean. Soil water status was monitored with tensiometer. Soil samples were taken along five transects perpendicular to the crop rows at 20-cm intervals, to a depth of 50 cm for bromide analysis. Sampling locations corresponded to row, quarter row, and interrow positions. In the fine sandy loam half of the corn plot there was significantly more leaching of bromide below the 50 cm depth in the interrow positions than in the row positions. This appears to be related to the soil water status since soil conditions in the corn plot were, on the average, drier under row positions than under interrow positions. In soybeans, differences in leaching between row and interrow positions were not significant in the fine sandy loam half. Overall leaching was less under soybean than under corn. Simplified two-dimensional simulations indicated that in the coarse textured area in corn, differences in water flux between row and interrow zones based on very small differences in evapotranspiration, on the order of 0.05 to 0.10 cm/d, result in differences between row and interrow bromide leaching which were in the range measured.

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## COMPARISON OF THREE FIELD METHODS TO CHARACTERIZE MACROPORE FLOW CAPACITY

TIMLIN DENNIS, AHUJA L J R, ANKENY M D

**Interpretive Summary:** Surface applied chemicals may bypass the soil matrix and move directly to ground water through large, continuous pores in the soil (macropores). Macropore flow capacity is a parameter necessary to simulate water and solute movement in soils with macropores. It is defined as the difference between hydraulic conductivity under ponded conditions and conductivity under a slight negative tension (3 to 8 cm). Conductivities under a slight tension were measured by infiltrating water through a thin crust and also obtained from measurements of water content during soil water redistribution. A tension infiltrometer was also used. Macropore flow capacities obtained from the crust or redistribution measurements were similar. Flow capacities from the tension infiltrometer were higher. The redistribution method is recommended since it is convenient and other hydraulic parameters can be obtained as well.

**Technical Abstract:** An objective of this study was to investigate several field oriented and non-destructive methods to characterize the flow properties of both the soil matrix and macropores. Soil matrix conductivities in eight 50-cm diameter rings were measured at tensions near saturation with a thin sand-cement crust and also estimated from redistribution measurements. These were compared to conductivities measured under ponded conditions using a double ring infiltrometer. Macropore flow capacity was obtained by difference. Matrix conductivities were also obtained using a 7.6-cm dia tension infiltrometer and ponded conductivities obtained from unconfined infiltration in similar-sized rings. Conductivities from the tension infiltrometer were higher than conductivities from the crust or redistribution methods probably due to a shallow restricting layer and the effect of air entrapment on confined measurements. Macropore flow capacities obtained using crust data were similar to those obtained from redistribution data. We concluded that macropore flow capacity can be characterized by using ponded infiltration rates and matrix conductivities near saturation determined from redistribution data.

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## VOLATILIZATION OF FONOFOS, CHLORPYRIFOS AND ATRAZINE FROM CONVENTIONAL AND NO-TILL SURFACE SOILS IN THE FIELD

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**Interpretive Summary:** No-tillage practices are being implemented by farmers in an effort to save energy and time, and reduce soil erosion losses. The most noticeable characteristic of a no-till field in comparison to a conventionally tilled field is the plant debris layer left on the soil surface. Because no-tillage fields are not plowed or disked fertilizer and pesticides are applied to the surface over the plant debris layer. A side-by-side field experiment compared pesticide loss by volatilization from a conventionally tilled plot and a no-till plot in a corn field. The plant debris layer on the no-till plot intercepted approximately 40% of the pesticide spray application. Volatilization losses of the more volatile pesticides were greater from the no-till plot than from the conventionally tilled plot. Increased pesticide loss by volatilization from no-till fields may create a need for higher application rates and perhaps lead to more environmental contamination by airborne pesticides. The results of this study suggest the need for different pesticide application techniques on no-till fields. The use of less volatile pesticides, more efficient application techniques such as injection beneath the soil surface, and more efficient pesticide formulations such as slow release pellets are possible solutions.

**Technical Abstract:** We measured the effect of no-till on pesticide volatilization by conducting a side-by-side comparison of volatilization rates from no-till (NT) and conventionally tilled (CT) fields. Volatilization rates were determined using the theoretical profile shape method for 10 of the 26 days following application. Soil and mulch residues were also evaluated. Volatilization losses of fonofos (O-ethyl S-phenyl ethylphosphonodithioate) and chlorpyrifos (O, O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) from the NT field were 2 to 4 times volatilization losses from the CT field. As much as half the application volatilized during 26 days. Volatilization of atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine -2,4-diamine) was also greater from NT, but only 1-2% of the application volatilized. Maximum volatilization rates were usually measured at mid-day, which suggests that volatilization was not limited by soil dryness. Over the 26 days of the experiment, volatilization decreased faster than pesticide residue was depleted, suggesting residues were becoming more strongly sorbed to soil and/or mulch, or were becoming less accessible to the surface.

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## EFFECT OF WATER POTENTIAL AND SOIL MICROBES ON RELEASE OF STARCH ENCAPSULATED ATRAZINE AND ALACHLOR

WIENHOLD BRIAN J, GISH TIMOTHY J

**Interpretive Summary:** Increased concern over the fate of agricultural chemicals has lead to the development of chemical formulations aimed at reducing the susceptibility of chemicals to leaching and volatilization. One such formulation involves encapsulating the chemical in starch. Starch encapsulation successfully controls the rate at which a chemical is released into the soil but little is known about the effect environmental factors have on the rate of release. The purpose of this study was to determine what effect water availability and soil microbial activity have on rate of release of starch encapsulated atrazine and alachlor. Results indicate that as availability declines rate of release also declines. Soil microbial activity increases the rate of release by digesting the starch matrix. Alachlor is released more quickly than atrazine most likely because alachlor is much more soluble in water than is atrazine. The environmental implication of these results is that controlled release reduces the susceptibility of chemicals to undesirable leaching and volatilization losses. The agronomic implication of these results is that complete release of starch encapsulated atrazine may not occur for several weeks under dry conditions. Hence, herbicidal activity may not be realized for several weeks after application and weed control may be reduced at early times.

**Technical Abstract:** This study was initiated to improve our understanding of how water potential and soil microbial activity influence rate of release of starch encapsulated atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) and alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide). Water potential, imposed using polyethylene glycol, significantly influenced swelling of the starch matrix and rate of release of both herbicides. At a water potential of 0 MPa, complete release required 21 days for atrazine and seven days for alachlor. As water potential declined so did rate of release. At a water potential of -1.5 MPa than 50% of the encapsulated atrazine and less than 80% of the encapsulated alachlor had diffused out of the starch matrix after 28 days. Soil microbes increase the rate of release. After 21 days there was a two-fold increase in the percentage of atrazine released from starch capsules applied to nonsterile soils compared to capsules applied to sterile soils. These results suggest that starch encapsulation is effective in controlling the rate of release of the herbicides used in this study, potentially reducing the susceptibility of these compounds to volatilization and leaching losses. However, full herbicidal activity may not be realized for 1 to 3 weeks after application when these herbicides are applied as starch encapsulated formulations.

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## EFFECT OF STARCH ENCAPSULATION AND TEMPERATURE ON VOLATILIZATION OF ATRAZINE AND ALACHLOR

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**Interpretive Summary:** Volatilization of agriculturally applied pesticides is one process whereby chemicals may enter parts of the environment where they were not intended, potentially exposing humans and sensitive crops to the chemical. This study was conducted to assess how starch encapsulation (SE) and temperature affect volatilization of two common herbicides when applied to moist soil at rates commonly recommended to farmers. Soil was maintained at three temperatures similar to those commonly encountered in the field. Soil covered the bottom of large glass chambers. Air inside each chamber was sampled continuously for 35 days to determine the amount of herbicide which volatilized from the soil. As temperature increased, volatilization of both herbicides also increased. Volatilization losses of alachlor were greater than those of atrazine at all temperatures. Volatilization of atrazine applied as SE formulation was less than when applied as emulsified concentrate. Volatilization of alachlor applied as SE formulation was greater than when applied as emulsified concentrate. These results will aid in determining whether SE will be a viable formulation modification for reducing environmental contamination by agricultural chemicals.

**Technical Abstract:** This study was conducted to assess how starch encapsulation (SE) and temperature affect volatilization of atrazine and alachlor using agroecosystem chambers as model systems. Herbicides were surface applied, at a rate of 1.7 kg/ha for atrazine and 2.8 kg/ha for alachlor, to the surface of moist soils maintained at temperatures of 15, 25 and 35 C. Air was drawn through the chambers (3.9 chamber volumes per minute) and any herbicide present in the vapor phase was trapped in polyurethane foam plugs. Plugs were replaced and herbicide mass trapped by the plugs determined 10 times during the 35 day experiment. Volatilization of both herbicides increased with temperature. Volatilization of atrazine was less when the chemical was applied as the SE formulation than when applied as emulsified concentrate (EC). After 35 days cumulative volatilization of atrazine ranged from < 1% of that applied as the SE formulation at 15 C to 14% of that applied as EC at 35 C. Volatilization of alachlor was greater when the chemical was applied as the SE formulation than when applied as EC. After 35 days cumulative volatilization of alachlor ranged from < 2% of that applied as either formulation at 15 c to 32% of that applied as the SE formulation at 35 C.

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## A DECISION SUPPORT SYSTEM FOR WATER QUALITY MODELING

YAKOWITZ D S, LANE L J, STONE J J, HEILMAN P, REDDY R K

**Interpretive Summary:** A prototype Decision Support System (DSS) has been developed to evaluate the environmental and economic consequences of alternative farming practices. This system of computer programs was developed to help protect our Nation's groundwaters and surface waters from potential contamination by fertilizers and pesticides used in agriculture. The DSS includes a simulation model to predict the effects of the alternatives and a decision model which ranks the feasible management practices. The method we have developed combines graphically based scoring functions and some simple linear programs to rank the alternative practices. This ranking is achieved in an objective manner under the guidelines of the decision maker. An example examining alternatives for a field near Tifton, Ga. illustrating the use of the system is presented.

**Technical Abstract:** A prototype Decision Support System (DSS) has been developed to evaluate the environmental and economic consequences of alternative farming practices. This system was developed to help protect our Nation's groundwaters and surface waters from potential contamination by fertilizers and pesticides used in agriculture. The DSS, with an embedded computer simulation model, ranks the feasible management practices using multiobjective decision theory. The method we have developed combines the use of graphically based scoring functions and some simple, yet powerful, linear programs to rank the alternative practices. This ranking is achieved in an objective manner under the guidelines of the decision maker. An example examining alternatives for a field near Tifton, Ga. illustrating the use of the system is presented. The prototype DSS is undergoing testing using data from several watersheds in the Deep Loess Soil Major Land Resource Area near Treynor, Iowa.

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## EVALUATING LAND MANAGEMENT EFFECTS ON WATER QUALITY USING MULTIOBJECTIVE ANALYSIS WITHIN A DECISION SUPPORT SYSTEM

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**Interpretive Summary:** A prototype Decision Support System (DSS) has been developed to evaluate the environmental and economic consequences of alternative farming practices. The DSS includes several computer simulation models to predict the effects of the alternative management systems and a decision model which ranks feasible management practices in order of preference. The ranking is achieved in an objective manner under the guidelines of the decision maker through the use of graphically based value functions and some simple mathematical programs. Testing of the prototype DSS using data from several watersheds in the Deep Loess Soil Major Land Resource Area near Treynor, Iowa has begun. An example application of the system applied to a field near Tifton, Ga. is presented.

**Technical Abstract:** A prototype Decision Support System (DSS) has been developed to evaluate the environmental and economic consequences of alternative farming practices. The DSS, with embedded computer simulation models, ranks feasible management practices using multiobjective decision theory. The method combines graphically based scoring functions and simple, yet powerful, linear programs to rank the alternative practices. This ranking is achieved in an objective manner under the guidelines of the decision maker. Testing of the prototype DSS using data from several watersheds in the Deep Loess Soil Major Land Resource Area near Treynor, Iowa has begun. An example application of the system applied to a field near Tifton, Ga. is presented.

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# AQUEOUS OZONOLYSIS OF S-TRIAZINES. I. DESCRIPTION OF ATRAZINE DEGRADATION PATHWAY AND PRODUCT IDENTIFICATION

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**Interpretive Summary:** Effective disposal of pesticide waste and equipment rinsate is desired to prevent contamination of groundwater and farm wells. A two stage process under investigation involves treatment of the waste with ozone followed by microbial degradation to give carbon dioxide, nitrogen, water and salts. Atrazine, one of the highest use herbicides, was found to be somewhat resistant to degradation relative to other pesticides. This study examined the overall mechanism by which ozone reacts with atrazine and the reaction products were isolated and characterized. Results demonstrated that the chlorine of atrazine was not removed and that the ring structure remained intact. This basic information is needed to further develop and optimize the waste disposal process.

**Technical Abstract:** The aqueous ozonation of atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) at pH 6 afforded four primary products: 6-amino-2-chloro-4-isopropylamino-s-triazine, 6-amino-2-chloro-4-ethylamino-s-triazine, 4-acetamido-2-chloro-6-ethylamino-s-triazine and 4-acetamido-2-chloro-6-isopropylamino-s-triazine. These compounds were subsequently degraded to 2-chloro-4,6-diacetamido-s-triazine, 4-acetamido-6-amino-2-chloro-s-triazine and 2-chloro-4,6-diamino-s-triazine. The amino alkyl groups are the first site of attack and are either removed or converted to the acetamide but not to the aldehyde. The s-triazine ring remains intact and the chlorine is not removed. Studies also demonstrated that the alkyl group is far more reactive than the amide moiety, which in turn is oxidized more rapidly than the amino group.

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